

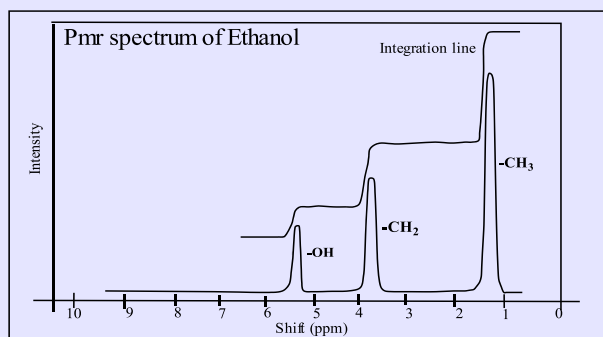
# Chemistry Revision Themes

## Part IIIb

Themes:

**Industrial Chemistry**

**Organic Analysis**



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(NB: Consult *your* examining board syllabus to establish precise requirements)

### Part IIIb:

#### Theme Fifteen: Industrial Chemistry

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#### Theme Sixteen: Organic Analysis

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Chromatography, Distillation & distillation theory, Qualitative analysis, Quantitative analysis, Mass spectrometry, Visible & Ultra-violet spectroscopy, Nuclear magnetic resonance spectroscopy, Gas chromatography & HPLC.

# Theme Fifteen

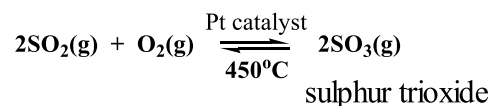
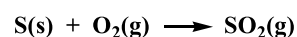
## Industrial Chemistry

### Sulphuric Acid (Sulphur(VI) acid)

It is a premier chemical in terms of the amount produced and the variety of other chemicals which require the acid for their manufacture.

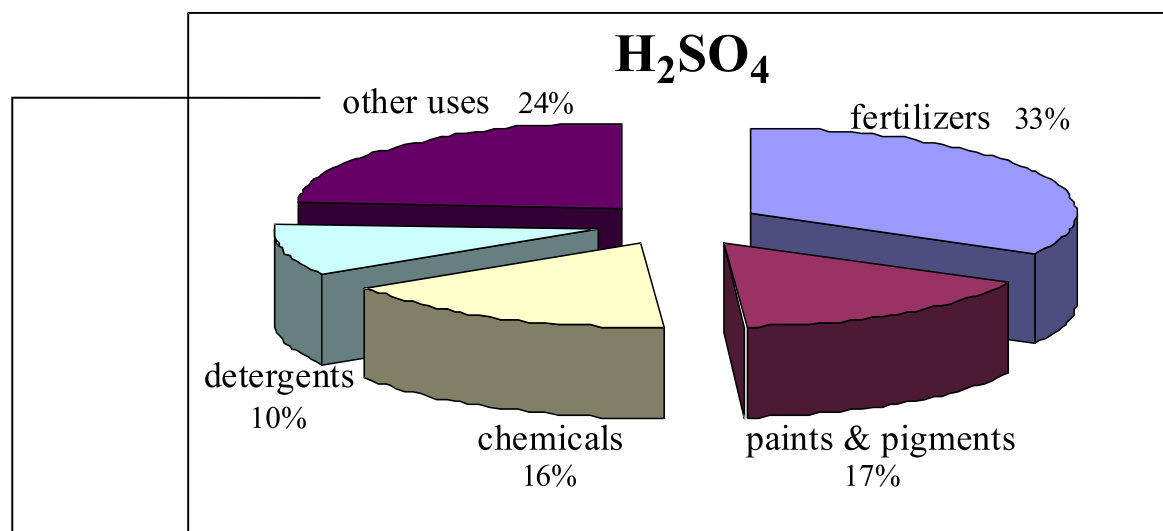
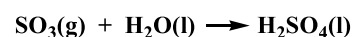
170 million tonnes per annum world-wide. 4 million tonnes are produced in the UK. This is sufficient to fill 2000 million 1 litre bottles!

You may remember that sulphuric acid is made by combining sulphur trioxide with water.  
ie,



What is all of this sulphuric acid used for?

The pie chart below gives the important manufacturing applications.



Other uses include,

- cleaning metals to remove oxide coat. The process is called 'pickling'.
- acid for car batteries.
- oil refining.
- anodising.

An example of pickling could be the removal of rust from the surface of iron.

ie,



## Agricultural Chemistry

As plants grow they take chemical nutrients from the soil.

The elements nitrogen, phosphorus and potassium are particularly important.

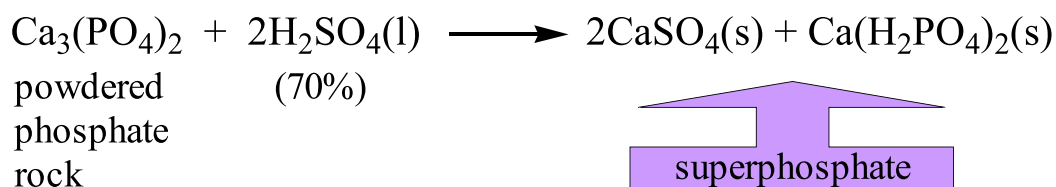
To ensure the soil contains sufficient of these, farmers apply synthetic, as well as natural, fertilizers to the land.

Potassium is provided by KCl mined in Yorkshire.

Superphosphate and various ammonium salts provide the elements phosphorus and nitrogen.

### Superphosphate

Made by,

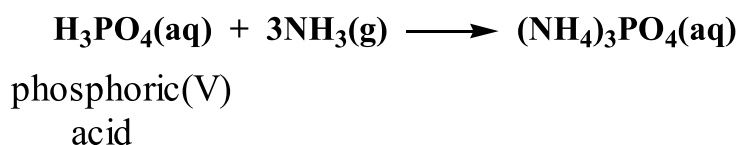


Unlike phosphate rock, the dihydrogenphosphate is soluble in water. It is washed into the soil when it rains and is taken up by the roots of the plants so providing the phosphorus they need.

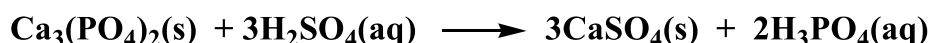
Phosphate rock is obtained from North Africa and Florida.

### Ammonium phosphate

Made by,



Phosphoric acid is made by treating calcium phosphate (from phosphate rock) with dilute sulphuric acid. Calcium sulphate is filtered off and the acid solution concentrated by evaporation.



Ammonium phosphate is an important fertilizer since it provides both nitrogen and phosphorus.

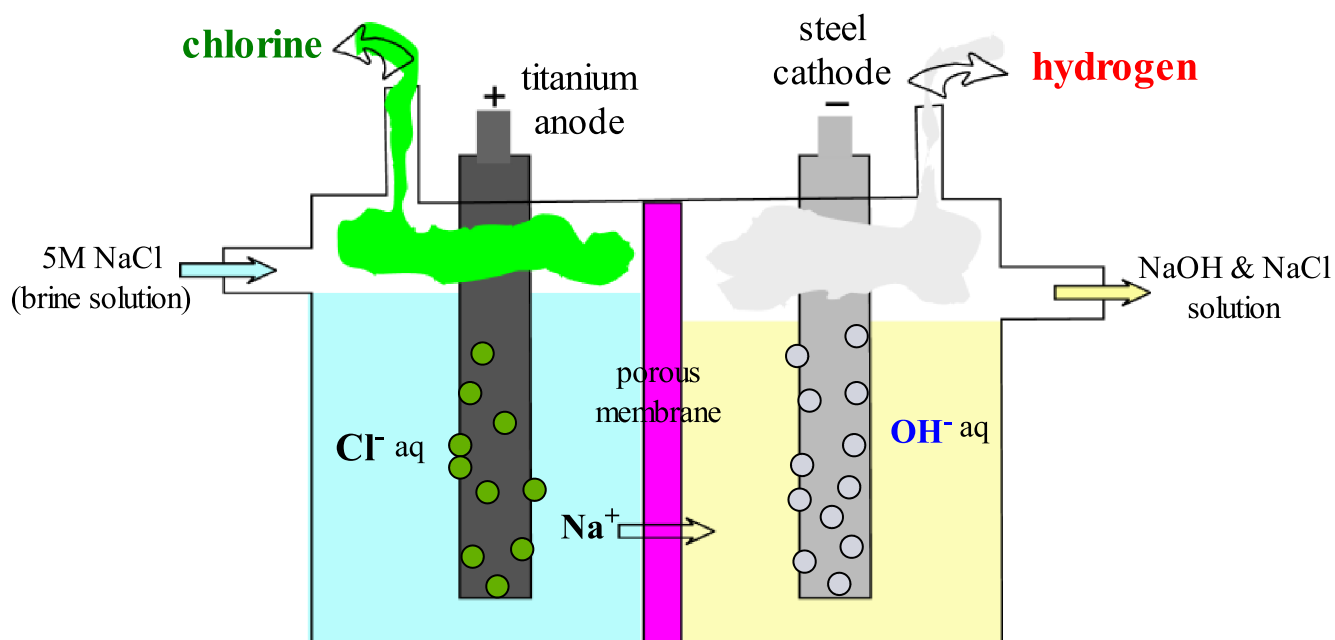


## Compound Fertilizer

Sometimes ammonia is neutralised with phosphoric acid and nitric acid. This gives a mixture of ammonium phosphate and ammonium nitrate. This mixture is an example of a *compound fertilizer* and is an excellent source of nitrogen and phosphorus.

## Chlorine

Manufactured by the electrolysis of sodium chloride solution in the, **membrane or diaphragm cell**.



The porous membrane is a synthetic fluorocarbon polymer which only allows small cations like Na<sup>+</sup> to pass through.

**The sodium ion is not discharged when it reaches the cathode. It is energetically easier to reduce water.**

ie,

**At the cathode (-):**



**At the anode (+):**



The overall result is that chlorine is generated in the anode compartment and hydrogen and sodium hydroxide are produced in the cathode compartment.

Sodium hydroxide solution is run from the cathode compartment along with unreacted sodium chloride. The two are separated by evaporation and cooling when the less soluble sodium chloride crystallises out and is filtered off.

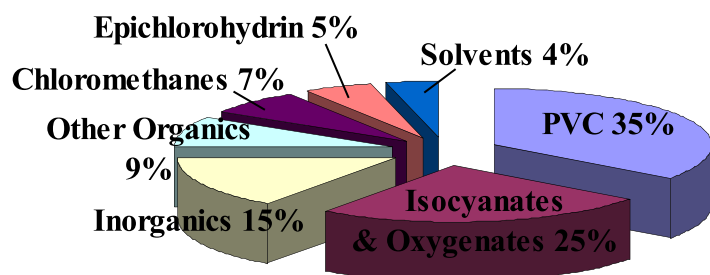
The final sodium hydroxide solution is about 12M and contains a small amount of sodium chloride.

Sodium hydroxide is an important industrial chemical (about 10 million tonnes/yr in Europe). It is used, for example, in the manufacture of soap & glycerol and to digest wood pulp in paper manufacture.

### Uses of Chlorine: (About 11 million tonnes /yr in Europe)

- Large amounts used to sterilise domestic water supplies including water for swimming pools.
- For bleaching wood pulp used in paper manufacture.
- For making chloroethene ( $\text{CH}_2=\text{CHCl}$ , vinyl chloride) which is the raw material for the manufacture of polyvinyl chloride (PVC).
- For making other organic chemicals which, in turn, are used to make drugs, insecticides, solvents and refrigerents.
- For making hydrogen chloride which is combined with water to give hydrochloric acid ( $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ ).
- For making sodium chlorate(I).

### Products manufactured using chlorine and chlorine containing compounds

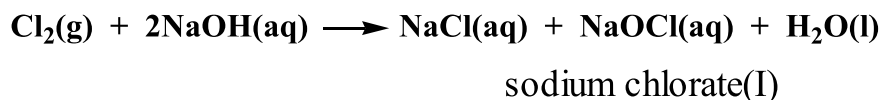


- (PVC 35%)** Pipes, flooring, medical supplies
- (Isocyanates & oxygenates 25%)** Upholstery, insulation, footwear, plastics, pesticides, car parts
- (Inorganics 15%)** Disinfectants, water treatment, paint pigments, silicon chips
- (Other organics 9%)** Detergents, ship and bridge paints, lubricants, wall paper adhesives, herbicides, insecticides
- (Chloromethanes 7%)** Silicon rubbers, decaffeinated, PTFE, paint strippers, cosmetics
- (Epichlorohydrin 5%)** Pesticides, epoxy resins, printed circuits, sport boats, fishing rods
- (Solvents 4%)** Metal degreasing, adhesives, dry cleaning, plastics

### Sodium chlorate(I) (sodium hypochlorite).

This is manufactured by electrolysis of a stirred brine solution.

Chlorine and sodium hydroxide are produced; they are mixed and allowed to react.

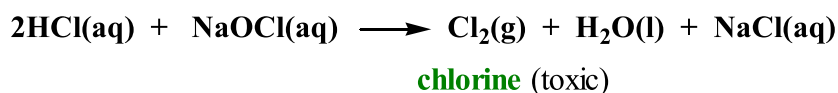


The resulting solution acts as a powerful **bleach** and is sold under brand names such as:

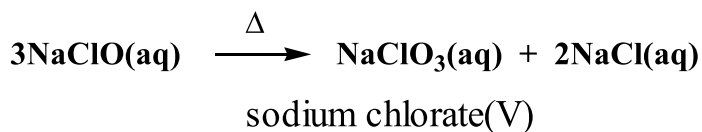
Milton, Domestos, and Parazone.

When bleach is treated with acid, chlorine is evolved.

It is important, when storing bleach and acid, to keep the containers well apart to avoid accidental mixing!



Sodium chlorate(I) *disproportionates* when its solution is heated.



Sodium and potassium chlorate(V) are used as powerful oxidising agents in the manufacture of matches and fireworks.

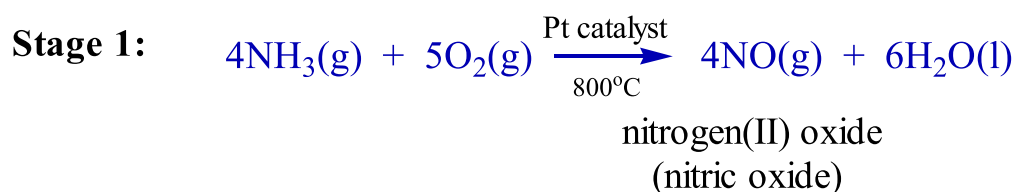
Sodium chlorate(V) has been used as a weed killer ; this application is now restricted.

Sodium chlorate(V) is made on a large scale by electrolysis of brine at about 75 degrees C and allowing the chlorine to react with the sodium hydroxide solution .

## Nitric acid

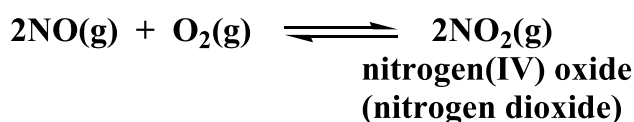
This is a **strong** acid. It is completely dissociated into hydrogen ions and nitrate ions in aqueous solution.

It is manufactured by oxidising ammonia. (The Oswald process; first used in 1908 in Germany)



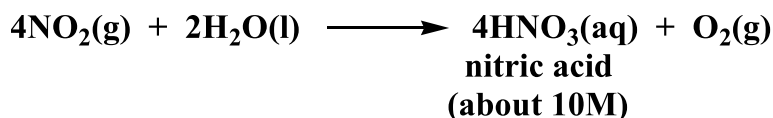
This reaction is exothermic ( $225 \text{ kJ mol}^{-1}$  of NO). Nitrogen(II) oxide is then cooled to about 150 degrees C and mixed with air in the next stage.

**Stage II:**



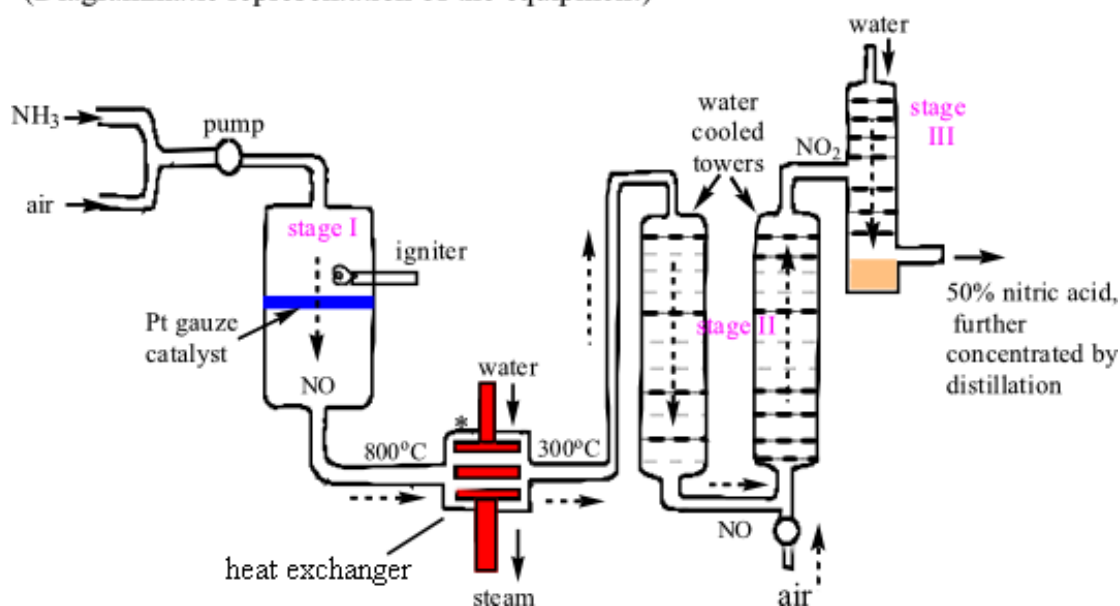
Nitrogen(IV) oxide is reacted with water in the next stage.

**Stage III:**



### Manufacture of Nitric Acid

(Diagrammatic representation of the equipment)



About 30 million tonnes of the acid is produced, annually, worldwide.

This compares with about 170 million tonnes of sulphuric acid and 9 million tonnes of hydrochloric acid.

About 75% of all the manufactured nitric acid is used to make nitrate fertilizers (mostly ammonium nitrate).

Other major uses include making dyes and explosives (such as trinitrotoluene).

Note:

(aqua regia (L. *royal water*): 25% concentrated  $\text{HNO}_3$  + 75% concentrated  $\text{HCl}$ . This will dissolve gold and platinum forming soluble chloro complexes.)

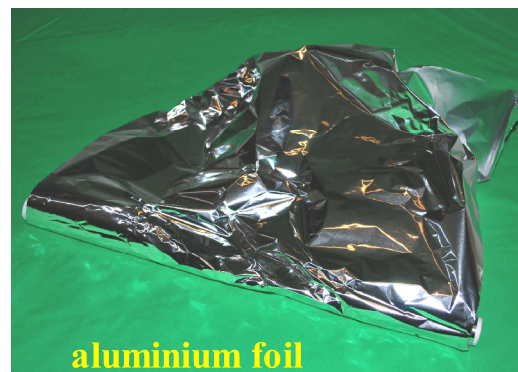
## Aluminium

Aluminium is the most abundant metal in the earth's crust (approximately 8%).

The majority of it is present in rocks and clay as complex aluminosilicates.

Because it is a reactive metal it does not occur in the free state in nature.

The metal is extracted from aluminium oxide which occurs naturally in an impure form called **bauxite**.



This is mostly  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and was so named because it was first mined in a district of France known as Les Baux.

There are large deposits of bauxite in Russia, Australia, Jamaica and Brazil.

### Extraction of Aluminium from Bauxite.

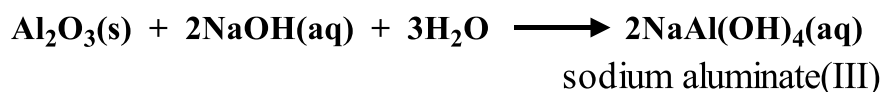
This is a two stage process:

1. **Purification** of bauxite to give alumina ( $\text{Al}_2\text{O}_3$ ).
2. **Electrolysis** of a solution of alumina in a mixture of molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) and aluminium fluoride ( $\text{AlF}_3$ ).

**Purification** is necessary because bauxite contains various other oxides which must be removed in order for the subsequent electrolysis to be successful.

In some cases the bauxite ore may contain as little as 50%  $\text{Al}_2\text{O}_3$  and possibly, 25%  $\text{Fe}_2\text{O}_3$  and variable amounts of  $\text{SiO}_2$  and  $\text{TiO}_2$ .

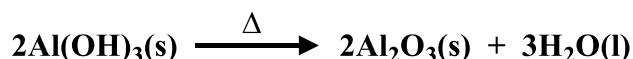
The bauxite ore is crushed and then digested with hot sodium hydroxide solution. The  $\text{Al}_2\text{O}_3$  reacts forming soluble aluminate.



The basic oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , do not dissolve in the alkali and can be filtered off.

The  $\text{SiO}_2$  is a slightly acidic oxide and reacts forming soluble silicate.

The alkaline solution is cooled, agitated with compressed air and seeded with a little aluminium hydroxide. This causes hydrated aluminium hydroxide to precipitate. It is filtered off and then heated to about  $1000^\circ\text{C}$  to drive off water and leave pure aluminium oxide (alumina).

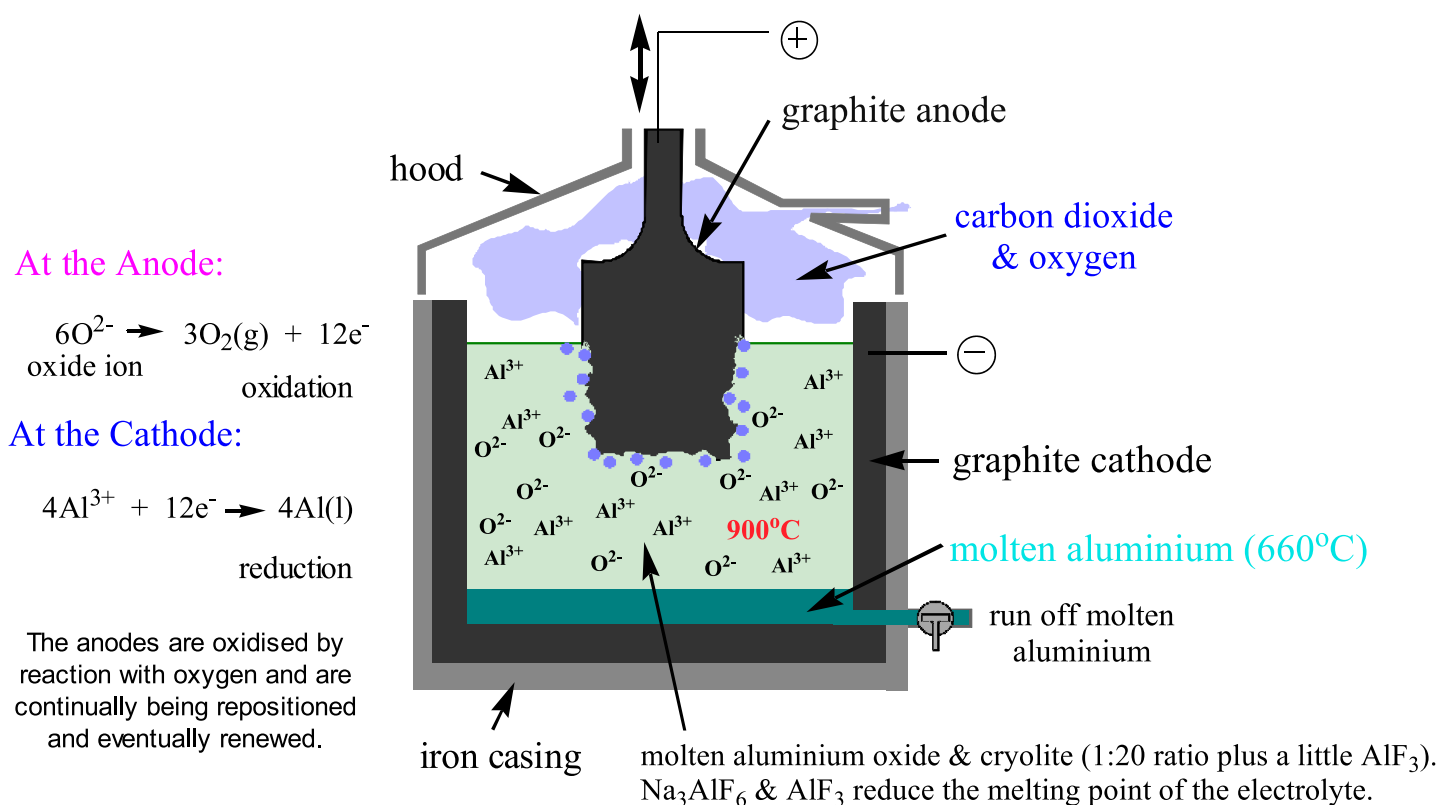


Silicon, as silicate, remains behind in the alkaline solution.

## Electrolysis of Aluminium oxide

About 15 000 kWh of electricity, 500 kg of carbon anodes and 50 kg of cryolite are required to produce 1 tonne of aluminium.

Low cost hydro-electric power is essential for the economic production of aluminium. The main producers are USA, Russia, Canada, Switzerland and Norway.



## Properties and Uses of aluminium:

About 20 000 000 tonnes of the metal are produced each year, worldwide.

It is expensive to make and to conserve natural resources we are encouraged to recycle the metal (eg, recycle drinks cans).

1. Aluminium has a very low density ( $2.7 \text{ g cm}^{-3}$ ) and is a fairly soft metal.

Alloyed with other metals it is used in the construction of cars, aircraft and ships.

eg, duralumin (Al(95.5%), Cu (3.5%), Mg (0.5%), Mn (0.5%) )

magnalium (Al(95%), Mg (5%) )

2. Aluminium is a good conductor of heat and electricity.

The metal is used to make cooking saucepans and electric power lines in the National Grid.

Large quantities of the metal are used in the food industry for making containers for convenience foods.

Aluminium foil is also used for protecting food (eg, chocolate).

3. Aluminium forms a tough protective oxide coat when exposed to oxygen (in air).

This gives the metal good corrosion resistance properties. The thickness of the oxide layer can be built up by an electrolytic process called **anodising**. The oxide coat can also be dyed a variety of colours.

4. Aluminium is an excellent reflector of heat and light.

It is used to make insulation blankets and reflecting telescopes (eg, 200 inch Hale telescope at Palomar mountain, in California and the Isaac Newton telescope now located at Las Palmas Observatory in the Canaries).

## Iron

Iron is a **transition element**. It is found in the centre block of the Periodic Table.

Fairly reactive metal, very little found in the free state. The metal is present in some meteorites.

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
57	72	73	74	75	76	77	78	79	80
La	Hf	Ta	W	Te	Os	Ir	Pt	Au	Hg

4th most abundant element in earths crust (6.2%); 2nd most abundant metal.

centre block of the Periodic Table



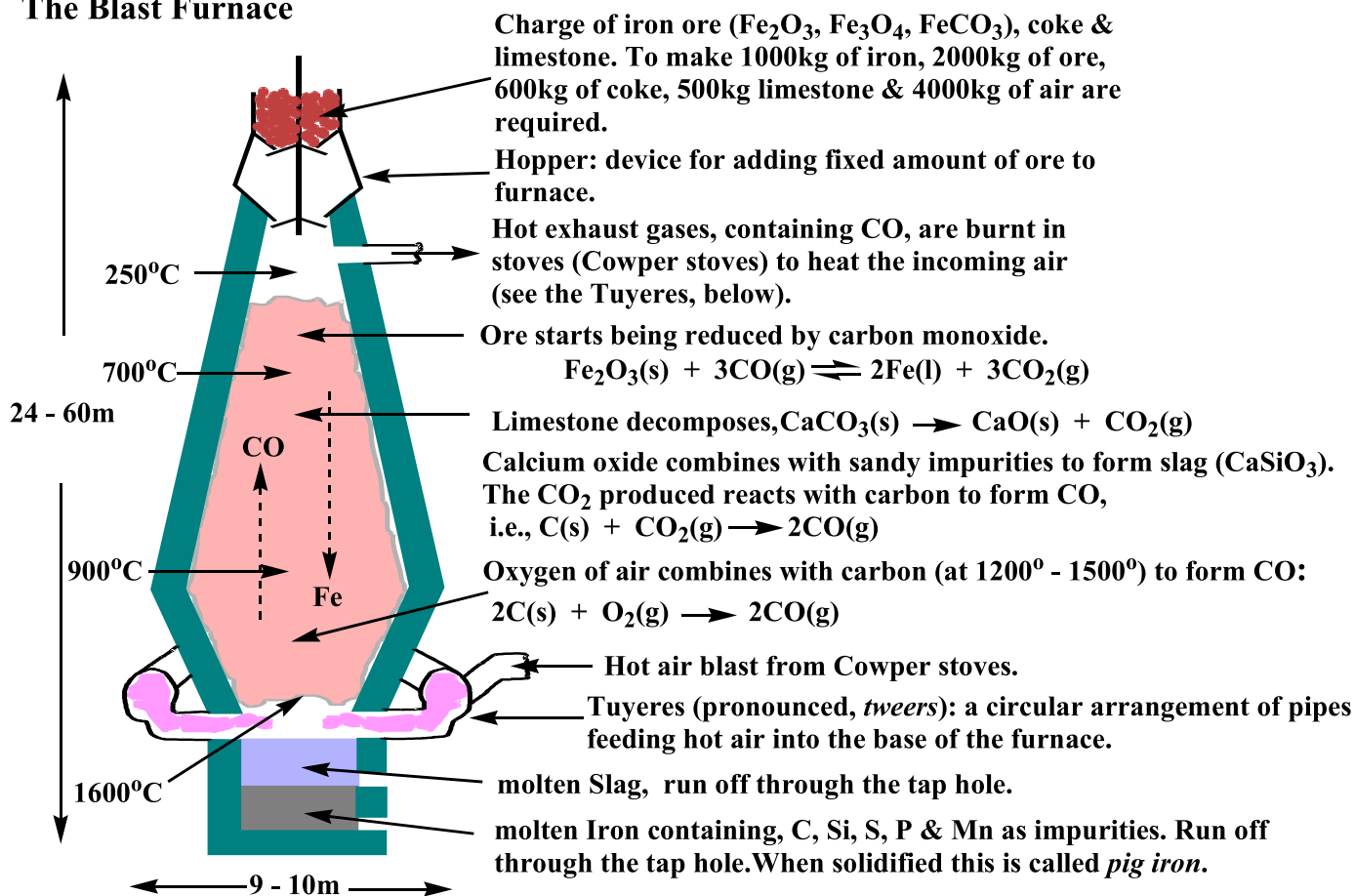
## Iron Ores



These ores are widely distributed over the earth's surface. Britain, Italy, Belgium, Germany, China, Brazil, Peru, Scandinavia, Russia and the United States of America have extensive deposits of iron ores.

Many of these countries extract the iron from the ores. The crude, extracted, iron is known as **pig iron**. Most of this is used to make **steel**. The extraction is performed in **blast furnaces**. An illustration of one type of blast furnace is shown below.

### The Blast Furnace





## Cast Iron

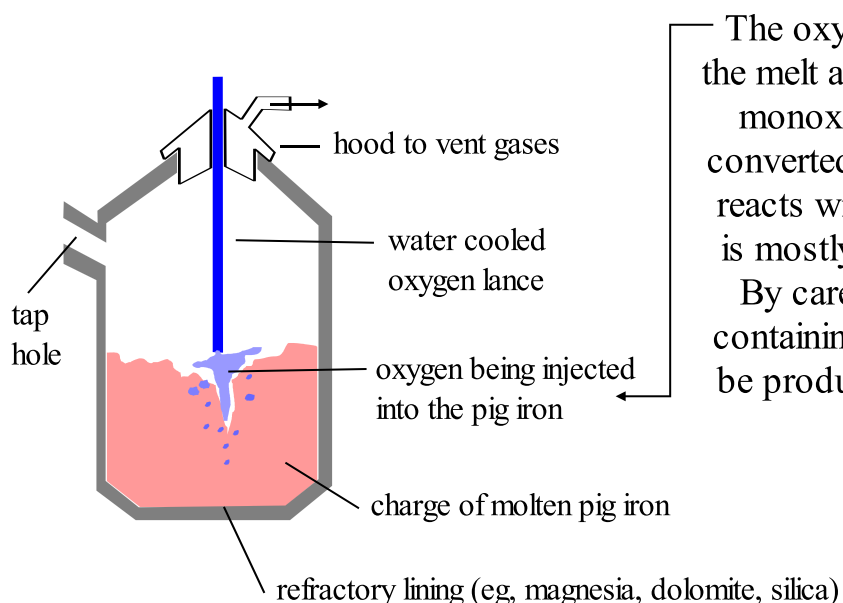
Cast iron is an impure iron made from pig iron and scrap iron. It melts at about  $1200^{\circ}\text{C}$  (compared with  $1539^{\circ}\text{C}$  for pure iron) and it is used for making castings since it has the property of expanding on cooling and therefore producing a good cast. Cast iron may contain as much as 4% carbon. It also contains sulphur, silicon and phosphorus and as a result of these impurities it is brittle.

## Wrought Iron

Wrought iron is a very pure iron. It is obtained from pig iron by heating with haematite. The haematite serves to oxidise the impurities so that they can be removed as slag or gas, e.g., carbon is converted to carbon monoxide and silicon and manganese are oxidised and removed as slag. Wrought iron melts at about  $1500^{\circ}\text{C}$  and it is ductile and malleable. It is used for making ornamental gates, chains, nails, agricultural implements, etc.

## Steel

Steel is produced from impure iron by reducing the carbon (from about 4% to 1%) and removing sulphur, phosphorus and silicon. A number of processes are available for making steel but the most widely used today is the **basic oxygen process (BOP)**. In this process, upwards of about 250 tonnes of molten pig iron (with a little added lime ( $\text{CaO}$ )) is introduced into a very large iron pot, similar in appearance to a **Bessemer converter** (named after Sir [Henry Bessemer](#), who was born in England, in 1813, but was of French descent), and injected with pure oxygen.



The oxygen forces its way into the body of the melt and oxidises excess carbon to carbon monoxide and carbon dioxide. Sulphur is converted to sulphur dioxide and phosphorus reacts with the lime to form basic slag which is mostly calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ). By careful monitoring of the process iron containing between 0.2 and 1.5% carbon can be produced to provide steel for a variety of applications.

**Steels** for a variety of applications :

**Mild steel** contains up to about 0.25% carbon and is ductile.

**Medium carbon steel** contains 0.25 to 0.45% carbon and is strong and hard.

**High carbon steels** contain up to 1.5% carbon and are very hard. Razor blades are made from this type of steel. Some applications of different types of steels are given in the adjacent table.

In addition to adjusting carbon content various other metals may be added to steel.

**Stainless steel**, for instance, contains chromium (15 - 25%) and nickel (7 - 12%) and sometimes molybdenum (1 - 3%). This type of steel has excellent corrosion resistance properties.

Type of Steel (%C)	Application
0.05	chains
0.2	ships hulls
0.25	bridges
0.35	axles
0.55	railway lines
0.9	tools
1-1.4	knives, scissors, chisels

Steels can be made very hard by heating to about 850°C and immersing in cold water.

Immersion in cold water is referred to as **quenching**. Steel treated in this way is hard but brittle. It can be made less brittle by further heating to 250°C and allowing to cool slowly. This is known as **tempering** or **annealing** the metal. Another way in which steel can be hardened is to incorporate manganese (10-15%) or titanium (1-5%) into the molten steel. This produces steel which is very difficult to cut with ordinary cutting tools. These alloy steels are used in the construction of aircraft and space craft and for making some railway lines, drilling, cutting, hammering and crushing machinery; also used for making prison cell gates and bars!

## Copper

Copper is another example of a **transition element** occurring in the centre block of the Periodic Table.

It is a fairly unreactive metal and has been found in the free state in nature. It has a characteristic reddish-brown colour.

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
57	72	73	74	75	76	77	78	79	80
La	Hf	Ta	W	Te	Os	Ir	Pt	Au	Hg

copper is a relatively scarce metal. It is the 25 th most abundant element in the earths crust (about 0.0034%) and the 17th most abundant metal.

Even though it is scarce, approximately 9 million tonnes of copper is produced annually world wide. It is likely that copper will become much more expensive as the existing ore deposits become depleted and the industry has to rely on less economic sources.

Copper ores are found in many parts of the world. At one time copper was mined in England and Wales and in the nineteenth century Swansea, in South Wales, was the major centre for the extraction and manufacture of copper. Today the major producers of copper are, USA, Russia, Chile, Canada, Zambia and Zaire.

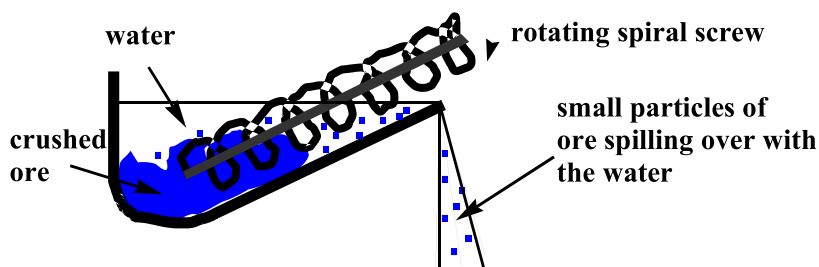
### Some copper ores



## The Extraction of Copper

### Stage 1: Crushing and Concentrating.

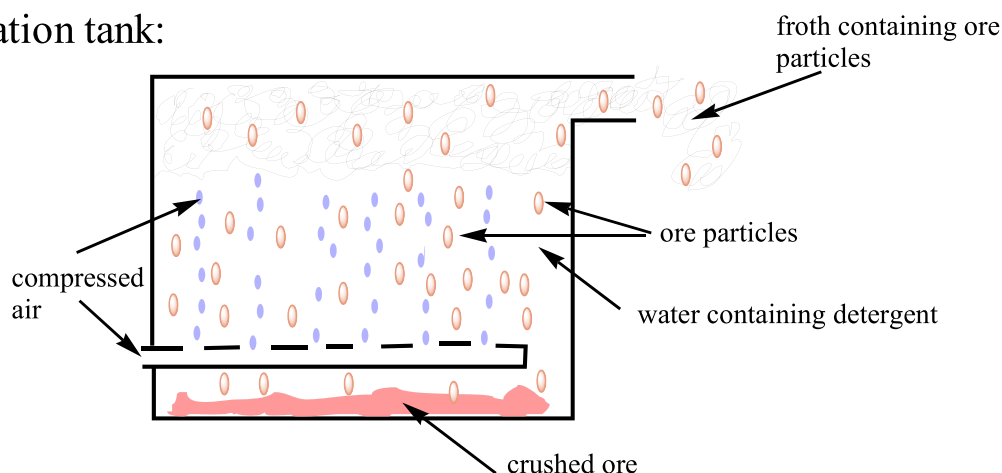
The ore is crushed in giant mechanical crushers and then concentrated in a device called a *spiral classifier*. This serves to separate small ore particles from larger rocks.



### Stage 2. Further Concentration:

In this stage the ore is agitated with water containing detergent. Froth is produced which serves to trap the small ore particles. Sand and other unwanted material tend to sink to the bottom of the *flotation tank*.

The flotation tank:

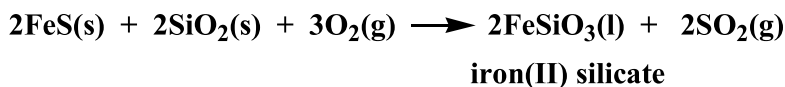


### Stage 3. Roasting in Air

Sulphide ores, such as copper pyrites, are roasted in air to convert to the simple metal sulphides.

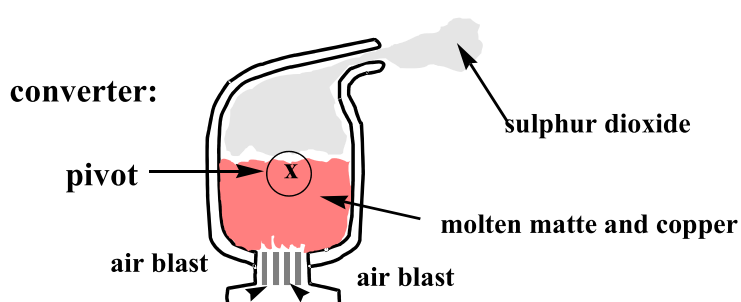


The sulphide mixture is then heated with limestone and/or sand when the unwanted iron is converted to slag (iron(II) silicate). This forms a separate layer, above the molten copper sulphide, and is removed. The molten copper sulphide is known as **copper matte**.

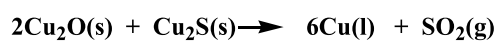


### Stage 4. Copper metal

The molten matte is introduced into a converter and air blasted for a number of hours.

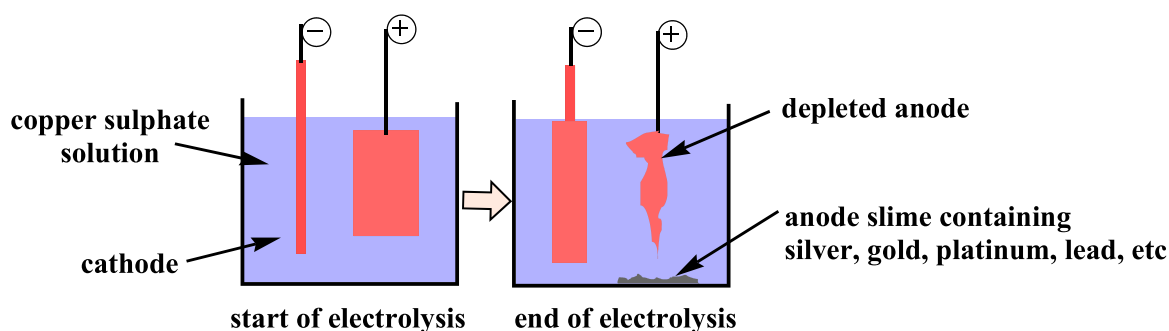


Exothermic reactions take place and the temperature rises to about 1300 °C. Copper(I) sulphide reacts with oxygen to form copper(I) oxide and this reacts with more copper(I) sulphide to give copper.



### Stage 5: Electrolytic Refining

Very pure copper is required for the electrical industry. This is made by the electrolytic purification of blister copper. Large blocks of blister copper are made the anodes in an electrolytic cell. The electrolyte is acidified copper(II) sulphate and the cathodes are sheets of pure copper. During electrolysis copper, from the anodes, goes into solution and is eventually deposited on the cathodes. When the cathodes reach a certain size they are removed and melted down and cast into ingots.



### Uses of Copper

Because copper is easily worked, it is an excellent conductor of heat and electricity, and can be alloyed with other metals it finds the following applications.

1. Unrefined copper is used to make copper pipe for conveying water and boilers for heating and storing hot water. It is also used as a roofing material.



2. The tensile strength of copper can be increased by alloying it with certain other metals. It forms brass when alloyed with zinc (3 parts copper, 2 parts zinc) and bronze when alloyed with tin and zinc (copper coins: 97% Cu, 0.5% Sn, 2.5% Zn).

Alloyed with nickel it is used to make silver coins. Nine carat gold jewellery is about two thirds copper.

3. It is used to make copper compounds.

4. As explained in a previous issue, copper forms a complex with ammonia ( $\text{Cu}(\text{NH}_3)_4^{2+}$ ). The solution of this complex ion finds application in the rayon industry since it is used to dissolve cellulose from which rayon is produced.

5. Large quantities of the electrolytically pure metal are used to make electric wire and various electrical components.

# Really Strong Metals

## Titanium & Tungsten

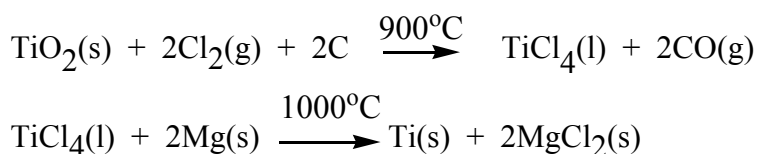
### Titanium (Ti)

Titanium is in the first transition series in the periodic table situated between scandium and vanadium. It was discovered as the dioxide by the English amateur geologist, William Gregor, in 1791. The pure metal was first prepared in 1910 by Matthew Hunter. It is the ninth most abundant element in the earth's crust (about 6%). Its main ores are ilmenite ( $\text{FeTiO}_3$ ) and rutile ( $\text{TiO}_2$ ). Its ores are widely distributed on earth and the metal has been detected in other parts of the universe.

It is a strong metal and has a high melting point ( $1667^\circ\text{C}$ ). Its density is nearly *half* that of iron. Its corrosion resistance is excellent (better than stainless steel and similar to platinum!). It has good resistance to the common acids. It is non magnetic.

These properties make titanium a valuable metal for, aircraft and spacecraft construction (its alloy with aluminium is particularly useful), ships components which are exposed to sea water, replacement hip joints (the metal has good compatibility with bone tissue) and jewellery (eg, wedding rings). The powdered metal is used in some fireworks to provide spectacular volcanic-like displays! The dioxide, which is white, is used as a paint pigment.

The metal is manufactured from its ores by first heating the ore (at about  $900^\circ\text{C}$ ) with carbon and chlorine to convert the metal to titanium(IV) chloride. This is a liquid and is distilled off. The chloride is then heated (at about  $1000^\circ\text{C}$ ) with either magnesium or sodium in an inert atmosphere (under argon). The resulting metal is leached with water to remove soluble salts (ie,  $\text{MgCl}_2$  or  $\text{NaCl}$ ). In the case of magnesium chloride it can also be removed by vacuum distillation.



Because the extraction/isolation process for producing titanium is involved and high tech the metal is expensive (about 15x more expensive than steel).

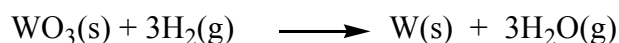
### Tungsten (W)

Tungsten (also known as Wolfram) is found between tantalum and rhenium in the centre d-block of the periodic table. It was discovered by Karl W Scheele in 1781. The metal was first extracted in 1783 by the Spanish d'Elhuyar brothers. It is the 56th (approx.) most abundant element in the earth's crust (about 1%). Its main ores are scheelite ( $\text{CaWO}_4$ ) and wolframite ( $(\text{Fe/Mn})\text{WO}_4$ ). These ores are widely distributed in the earth's crust.

It is a strong metal and has a very high melting point ( $3422^\circ\text{C}$ , the highest of all the metals). The pure metal is ductile so that it can be drawn out into thin wire suitable for electric light filaments. The metal is alloyed with iron to make very hard steels suitable for making cutting tools and armaments. It is also very heavy, nearly as dense as gold ( $\text{Au} = 19.30 \text{ g per cm}^3$ ,  $\text{W} = 19.25 \text{ g per cm}^3$ ). Because it is so dense it is used to make fishing line weights.

The metal is also converted to tungsten carbide (WC) by heating with carbon at about  $1800^\circ\text{C}$ . The carbide is heavy and very hard and is used as an abrasive. Both the metal and its carbide are used to make jewellery. Like titanium, tungsten is an expensive metal.

The metal can be manufactured from scheelite by digestion in hydrochloric acid (about 20%) and some nitric acid. The solid residue is tungstic acid ( $\text{H}_2\text{WO}_4$ ) which is taken up in ammonia solution. This ammonium tungstate solution is treated with hydrochloric acid to about pH 7 when ammonium paratungstate ( $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 11\text{H}_2\text{O}$ ) is precipitated. This is filtered off and heated at about  $650^\circ\text{C}$  to give tungsten(VI) oxide. The oxide is heated in a stream of hydrogen at about  $700^\circ\text{C}$  to give the metal. The hydrogen stream removes water in the form of steam. Water is condensed and the excess hydrogen recycled. Great care is taken to ensure that oxygen is excluded from the process to avoid explosion with hydrogen!



(As far as GCE exams are concerned this reduction stage is, at present, the only part of the extraction process which is important!)



# Theme Sixteen

## Organic Analysis

### 1. Over-view

(i) The first stage in the analysis of an organic substance is to establish whether it is a single substance or a mixture.

A pure organic compound will melt and boil *sharply*. Mixtures melt over a range of temperature.

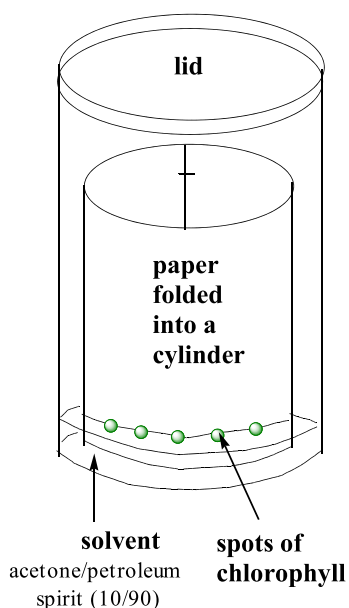
Melting points and boiling points are so called *criterion of purity*.

The purity of a compound can be confirmed by *chromatography*.

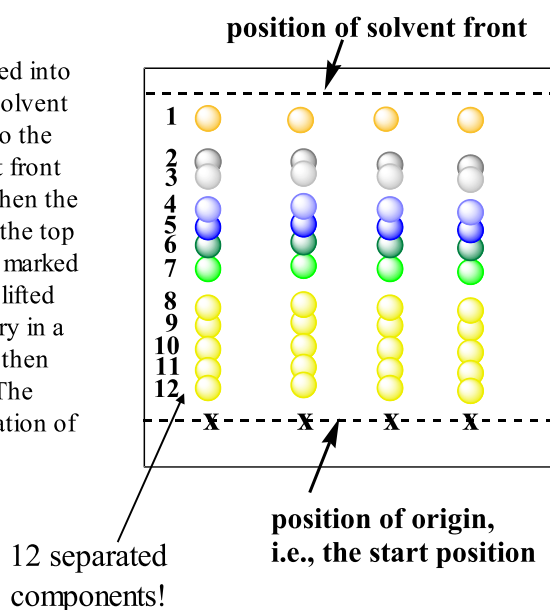
This involves washing a small sample of the substance through a stationary separation medium using liquid or gaseous fluids.

In the simplest case the sample is applied to *chromatography paper* and the paper *eluted* with a liquid solvent. The sample is carried along behind the solvent front and if it is impure it separates into a series of spots corresponding to each of the components. If the components are coloured they will be visible to the naked eye and can be assessed in terms of number and quantity. Alternatively, if they are colourless they can be visualised by spraying the paper with a suitable locating agent.

eg, **chlorophyll** - extracted from plant material using propanone (acetone); the extract is concentrated by evaporation and applied to the paper.

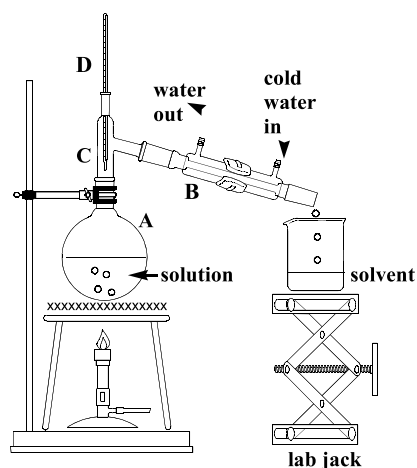


Once the paper has been lowered into the tank and is dipping in the solvent mixture, the solvent soaks into the absorbent paper and a solvent front moves, slowly, up the paper. When the front is within about an inch of the top edge of the paper its position is marked with a pencil and the paper is lifted from the tank and allowed to dry in a fume cupboard. The paper is then opened out and examined. The adjacent diagram is a representation of the expected result.

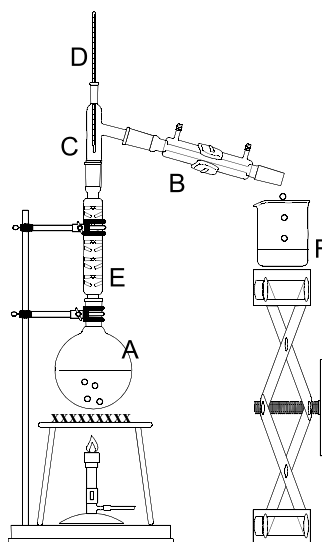


(ii) The second stage involves purifying the sample. There is little point in performing analysis on a mixture; the results would be ambiguous and very confusing. A number of methods are available for purification.

eg,



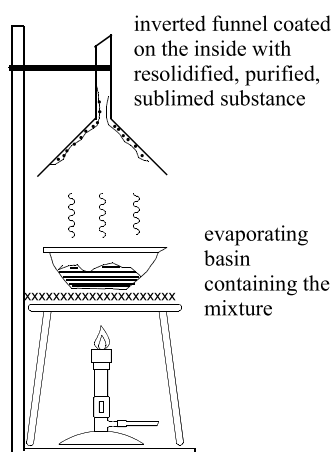
**simple distillation** - suitable for separating liquids with quite different boiling points



**fractional distillation** - suitable for separating complex liquid mixtures. The components have a range of boiling temperatures

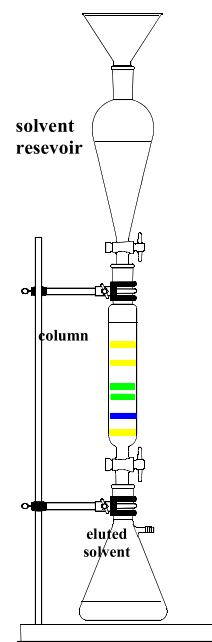
- A = distillation flask
- B = water condenser
- C = still head
- D = thermometer
- E = fractionating column

## The theory of distillation is covered in the following pages



**sublimation**

**Recrystallisation** - this is a technique which is used to remove small quantities of contaminants from natural or synthetic organic, crystalline, material. The impure solid is dissolved in the minimum of hot solvent and the solution allowed to cool (ice cooling may be necessary). Purified material crystallises from solution and is filtered off and dried. Impurities remain behind in the filtrate.



Column chromatography - the illustration shows the separation of the components of chlorophyll. The individual components are collected as they are washed from the column into receiving flasks. High performance liquid chromatography (HPLC) is another separation method which is referred to later.



## Distillation of two miscible liquids.

### Terms:

**Boiling point:** This is the temperature at which boiling occurs.

At this temperature the pressure exerted by the molecules of the liquid equals the external pressure (atmospheric pressure). Bubbles of vapourised liquid form in the body of the liquid.

The pressure exerted by the boiling liquid is the sum of the partial pressures of the constituents.

ie,

Total external pressure ( $P_T$ , atmospheric) =  $P_A + P_B$  where A and B refer to the constituents.

The process by which a liquid is boiled and its vapour collected and condensed back into liquid is known as **simple distillation**. **Fractional distillation** is where distillation is repeated many times in a column known as a fractionating column. Use of the fractionating column is equivalent to performing a large number of simple distillations connected in series. Fractional distillation generally gives a much better separation of the components of the mixture. Distillation is used for separating volatiles from non-volatiles (eg, purification of water) and separating mixtures of miscible liquids (eg, methanol and water).

### Theory:

Suppose the mixture is comprised of liquids A and B.

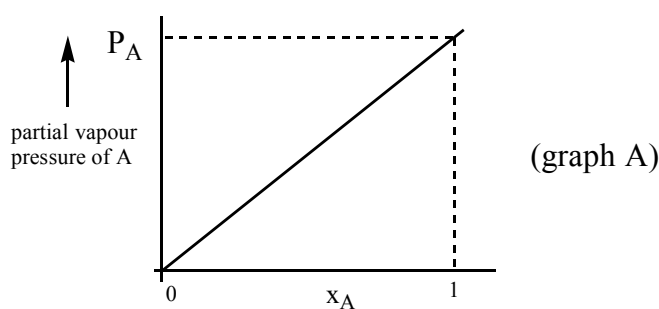
If the molecules of A and B are similar in size and exhibit similar forces of attraction (ie, intermolecular forces) then the effect of mixing A with B is simply a diluting effect. For a simple case like this the partial pressure of A in the vapour above the mixture is given by,

$$P_A = x_A \cdot P_A^0$$

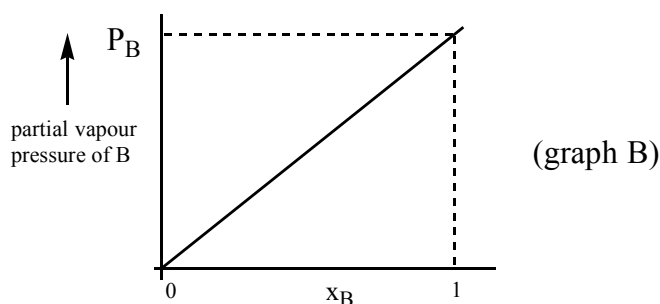
This is a statement of **Raoult's law**.

Where,  $x_A$  = mole fraction of A in the liquid mixture,  $P_A^0$  = vapour pressure of pure A at the same temperature as the mixture,  $P_A$  = partial vapour pressure of A (in the vapour above the mixture of A and B). ( $x_A$  = moles of A in mixture / (moles of A + moles of B) )

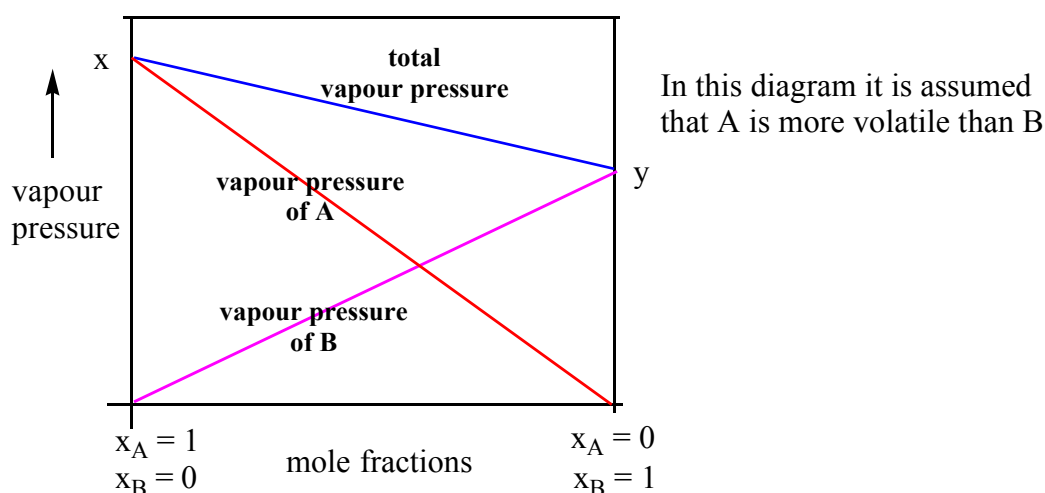
The equation may be expressed graphically,



Similarly for component B,  $P_B = x_B \cdot P_B^0$

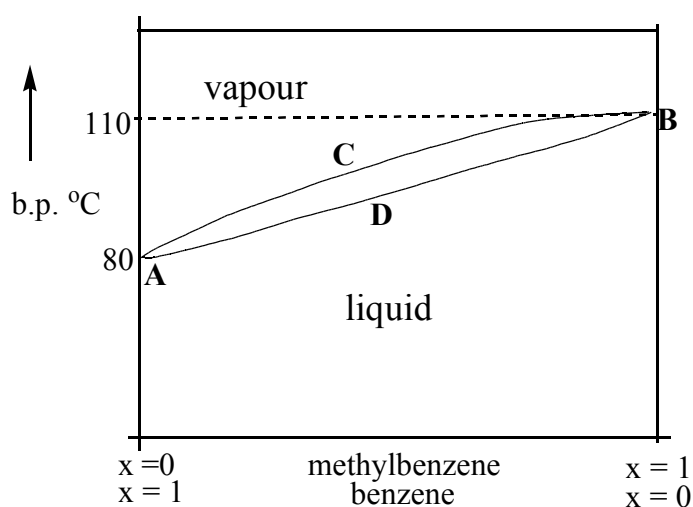


The graphs A and B can be combined onto one set of axes.



Since the vapour pressure of a liquid mixture varies with the composition of the mixture (as shown in the previous graph), the boiling point of mixtures of different composition will vary in similar fashion. Remember, a liquid boils when its vapour pressure equals the external pressure (eg, atmospheric pressure).

eg, the benzene/methylbenzene boiling point composition diagram:

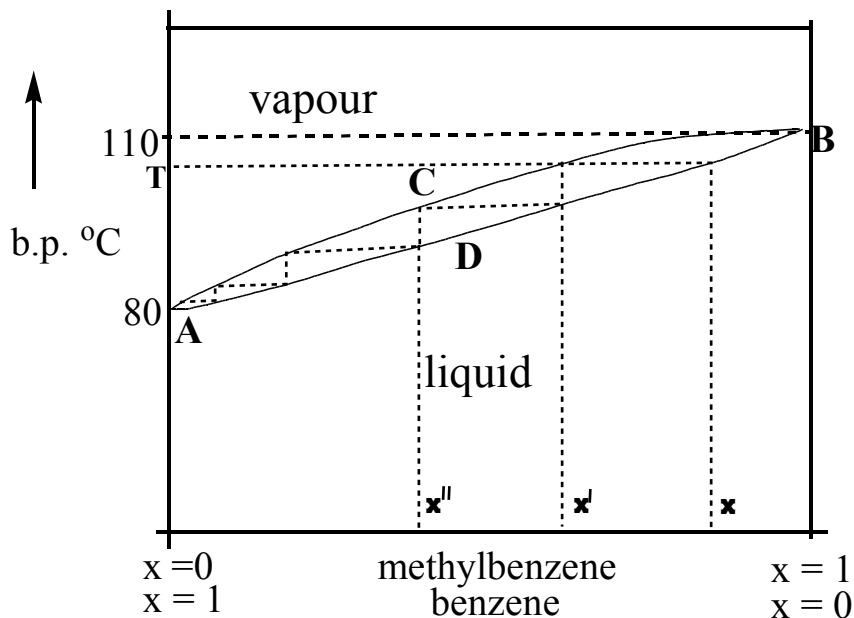


In the diagram, line ACB shows the composition of the vapour above the boiling liquid.

Line ADB shows the composition of the boiling liquid (ie, liquid remaining below the vapour).

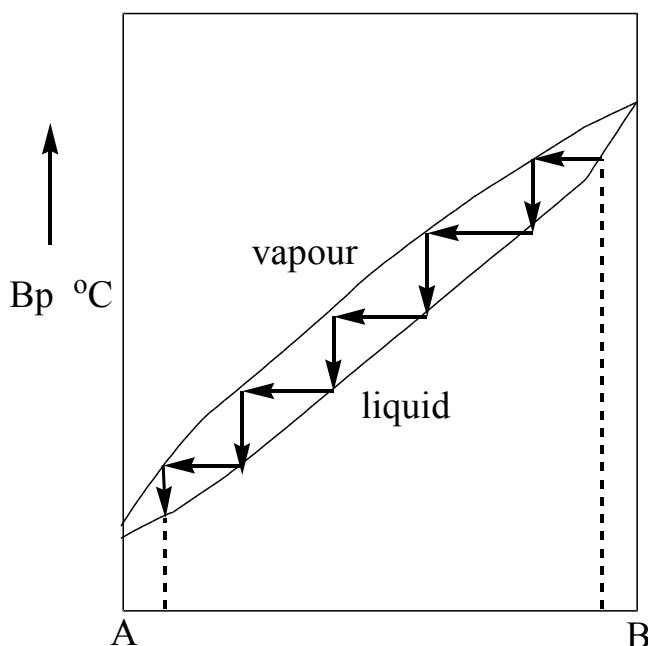
The diagram can be used to illustrate what happens when the methylbenzene/benzene mixture is, (a) subject to simple distillation and (b) subject to fractional distillation.

A liquid mixture of composition  $\mathbf{x}$ , will boil at temperature  $T$  (about  $105^{\circ}\text{C}$ ) and produce a vapour of composition  $\mathbf{x}'$ . This condenses to produce a liquid of the same composition  $\mathbf{x}'$ . If this liquid is boiled it will produce a vapour of composition  $\mathbf{x}''$  which will condense to a liquid having the same composition ( $\mathbf{x}''$ ). Step  $\mathbf{x}$  to  $\mathbf{x}'$  corresponds to simple distillation. Steps  $\mathbf{x}$  to  $\mathbf{x}'$  to  $\mathbf{x}''$ , etc, correspond to fractional distillation.



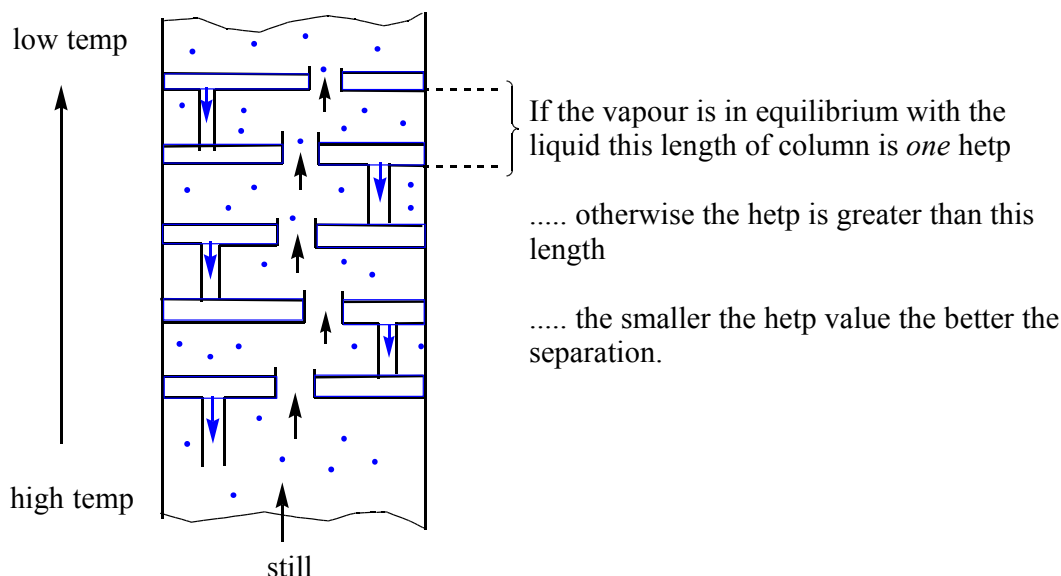
In an industrial fractionating column (eg, plate and bubble-cap type as used in the petroleum industry), a large number of distillation steps are involved.

eg,



Each step (corresponding to each horizontal line on the diagram) is counted as a theoretical plate and the number of steps from the composition of the original liquid to that of the final distillate gives the number of theoretical plates for this separation (just five indicated in the diagram). The more theoretical plates the better the separation. Sometimes the performance of a fractionating column is expressed in terms of the height equivalent to a theoretical plate (HETP). This is defined as: *the length of column, from the top of which rises a vapour of composition in phase equilibrium with the liquid leaving the bottom.*

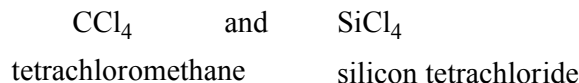
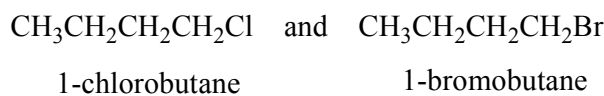
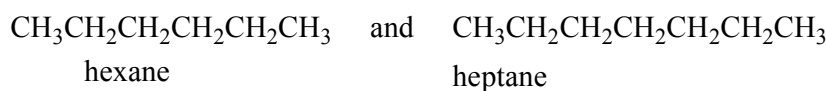
Part of a bubble-cap column:



### Deviations from Raoult's Law

Liquid mixtures which behave as described previously and obey Raoult's law are said to be **ideal**. Compounds with molecules of similar size and polarity form ideal mixtures.

eg,



Most liquid mixtures deviate to some degree from the ideal; they show either positive or negative deviation.

#### Positive deviations:

Vapour pressure exerted by the mixture is **greater than** expected.

Molecules of A (or B) escape more easily from the mixture A/B than from pure A (or pure B).

This means that forces of attraction between like molecules is greater than between unlike molecules.

Examples: ethanol - water and tetrachloromethane - ethanol.

Excessive positive deviation results in the mixture forming two layers and absorbing heat (endothermic change).

#### Negative deviations:

Vapour pressure **less than** expected.

Molecules of A (or B) escape less easily from the mixture A/B than from pure A (or B).

This means that forces of attraction between like molecules is less than between unlike molecules.

Example: water - hydrogen halide (HX) & trichloromethane- ethyl ethanoate.

Negative deviations are less common than positive deviations.

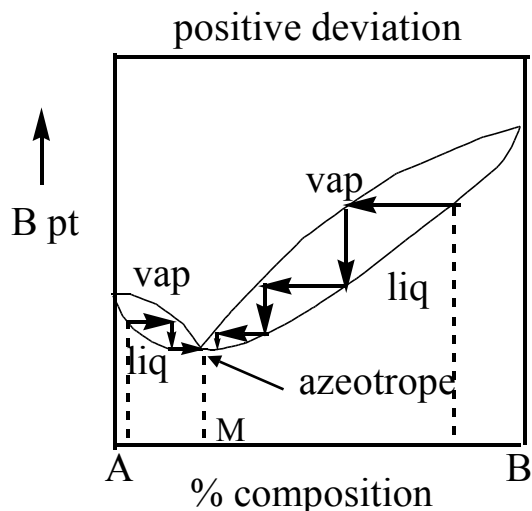
Excessive negative deviation results in formation of compounds between A and B. There is also exothermic change.

The boiling point - composition curve for a mixture showing positive deviation has a minimum corresponding to a constant boiling mixture (an azeotrope - from the Greek meaning *boiling without change*). The boiling point - composition curve corresponding to negative deviation shows a maximum.

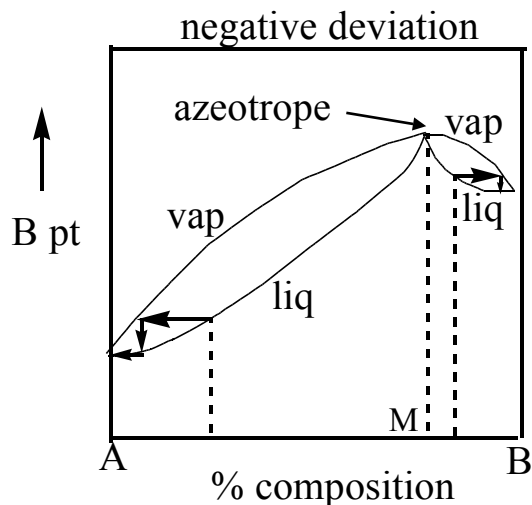
eg,

The boiling point - composition curve for a mixture showing positive deviation has a minimum corresponding to a constant boiling mixture (an azeotrope - from the Greek meaning *boiling without change*). The boiling point - composition curve corresponding to negative deviation shows a maximum.

eg,



**The distillate approaches the composition of the azeotrope. The residue approaches either A or B.**



**The distillate approaches either A or B. The residue approaches the azeotrope.**

A mixture of ethanol and water exhibits positive deviation. If any mixture of ethanol and water is fractionally distilled, the distillate will be an azeotrope consisting of 89.4% ethanol and 10.6% water. This mixture boils at a constant temperature of 78.2°C.

In order to isolate pure ethanol from this azeotrope it is necessary to distil from calcium oxide. The latter takes up the water. Alternatively, benzene can be added and the mixture distilled. Ethanol, water and benzene distil off together (as a ternary azeotrope) followed by a mixture of ethanol and benzene (as a binary azeotrope) and finally, pure ethanol distils over.

(iii) The third stage involves detailed analysis of the purified, *single, substances*.

## 2. Analysis of the isolated, pure, organic compounds.

Having carried out preliminary analyses and, where necessary, separated the original sample into major and minor constituents, the individual, pure, components can be identified.

### (i) Qualitative Analysis.

Establishing the *element composition* of a pure compound.

**Carbon:** heat a sample with powdered copper(II) oxide. If carbon is present it will be oxidised to carbon dioxide which can be identified with lime water (turns milky!).

**Hydrogen:** if this is present, heating with copper(II) oxide produces water vapour which can be tested for with anhydrous copper sulphate (turns blue) or anhydrous cobalt chloride (turns blue to pink).

**Halogen, nitrogen and sulphur:** strongly heat a sample of the substance with metallic sodium. Halogen is converted to halide ion, nitrogen is converted to cyanide ion and sulphur is converted to sulphide ion. These ions are then identified by simple inorganic analysis. The whole procedure is often referred to as the **Lassaigne sodium fusion test** (after the French chemist Jean Louis Lassaigne 1800-1856).

The ion mixture is taken up in distilled water and the solution divided into three portions. One portion is tested for halide ion with silver nitrate and dilute nitric acid. Silver halide precipitates are formed if halide ion is, indeed, present.

A second portion is treated with iron(II) sulphate and the mixture boiled. A drop or two of iron(III) chloride and a few mls of dilute sulphuric acid are added. The mixture is filtered and specks of solid **prussian blue** ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ) identified. If this complex is observed it establishes carbon and nitrogen in the original substance.

To a third portion is added a dilute solution of sodium nitroprusside ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ ). An immediate reddish-purple colouration confirms sulphur.

If carbon and hydrogen are present the organic nature of the substance is established. If nitrogen is present the substance may be an amine, amide or nitrile. If it contains halogen as well as nitrogen it may be an amine salt. If nitrogen is absent it may be an acid, acid anhydride, aldehyde, ketone, alcohol, ester or carbohydrate.

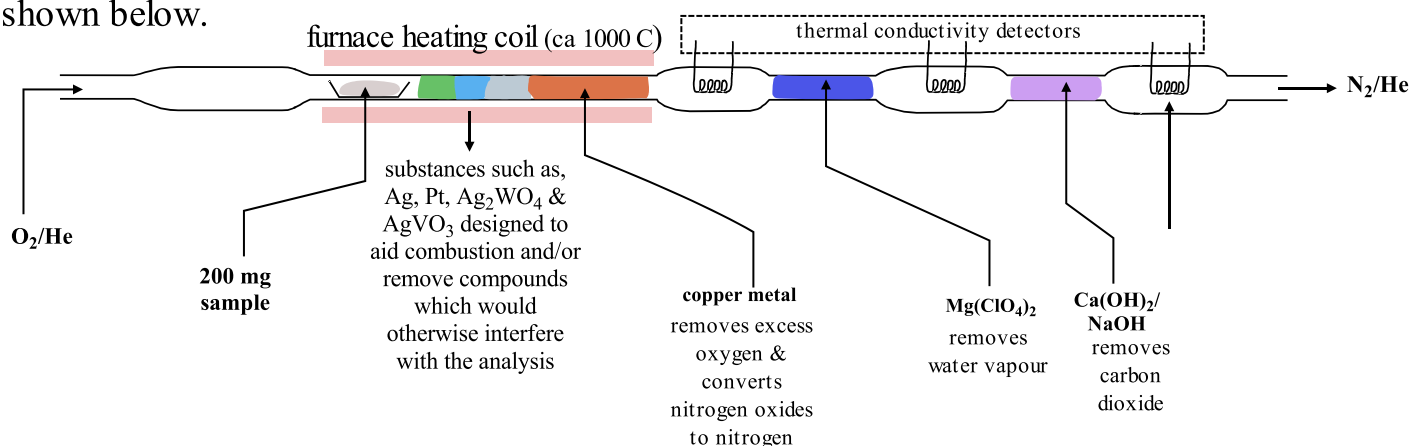
A variety of simple qualitative tests (like those describe in issues 10, 11, 12) can be applied to the substance to establish which if these functional groups are present in its molecules.

Following *qualitative analysis* it is possible say whether the substance is complex or simple and which functional groups it contains. However, it is not possible to identify the substance solely on the basis of qualitative analysis results. To identify the substance unambiguously it must be analysed *quantitatively*, to provide its relative molecular mass, and spectroscopic techniques must be used to confirm functional groups and the overall molecular structure.

### 3. Quantitative Analysis.

#### (a ) Percentage composition of the elements by Chemical analysis.

The traditional quantitative method of analysing a pure organic substance for the elements, carbon, hydrogen and nitrogen, involves combusting a small amount of the substance (eg, 200 mg) in a helium-oxygen rich mixture. A simplified diagrammatic representation of the process is shown below.



Burning the organic compound in oxygen produces a number of gaseous, oxidation, products. All are removed in the heated section *except* carbon dioxide, steam (water vapour) and nitrogen. These are then determined by measuring the thermal conductivity of the gas stream before and after removing individual gases. In the case of nitrogen, a comparison is made of the thermal conductivity of the gas stream containing nitrogen with that containing pure helium. The apparatus can be calibrated by combusting ultra pure standard substances containing the elements of interest. The thermal conductivity measurements are converted into masses of carbon dioxide, steam & nitrogen and from these the percentages of carbon, hydrogen and nitrogen, in the original 200 mg sample, calculated. A number of designs of apparatus are available. For example, gas liquid chromatography (glc) with a thermal conductivity detector can be used to separate and estimate the combustion products. The apparatus can also be modified for the estimation of sulphur (as  $SO_2$ ) and chlorine (as  $HCl$ ).

(Sulphur and halogen have been estimated in organic compounds by the **Carius Method** (after Georg Luddwig Carius 1829-1875): Sulphur was determined by heating a small sample of the pure compound with concentrated nitric acid and barium nitrate in a sealed tube (Carius tube). The sulphur is converted into barium sulphate. The tube was opened and washed out with distilled water. The solution was filtered to isolate barium sulphate. The sulphate was dried and weighed. The corresponding amount of sulphur was calculated.

Halogen was determined by heating a sample with concentrated nitric acid and silver nitrate. Silver halide was filtered off, dried and weighed. The corresponding amount of halogen was calculated.)

Having completed qualitative and quantitative analyses for the element the empirical formula can be deduced.

eg,

An organic compound was found to contain 12.77g of carbon, 2.13g of hydrogen and 85.1g of bromine in every 100g.

<b>C</b>	:	<b>H</b>	:	<b>Br</b>
12.77/12		2.13/1		85.1/80
1.064		2.13		1.064
1		2		1

ie, CH<sub>2</sub>Br

The next step is to work out the molecular formula of the organic compound. To achieve this the *relative molecular mass* is required. A number of methods are available for determining this. The method of choice is **mass spectrometry**. Using this technique (introduced in issue 1) the relative molecular mass was found to be 188. Comparing this value with the formula mass of the empirical formula it is clear that the molecular formula of the organic compound is C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>.

## (b) Mass Spectrometry.

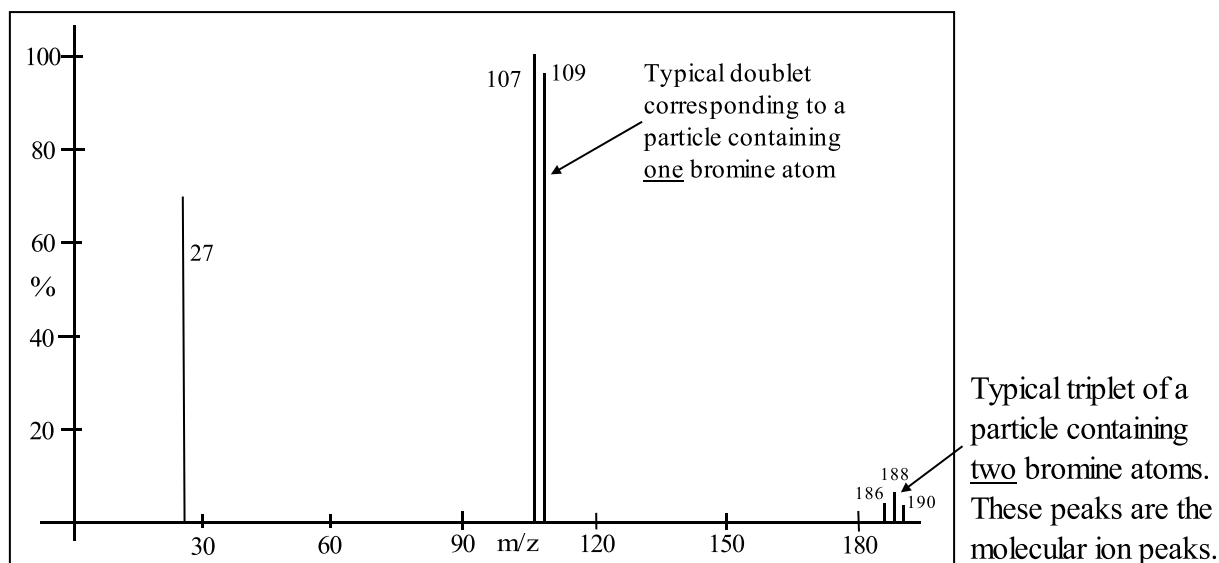
This instrumental method can identify the elements by their particle masses and isotope patterns. It is also capable of giving the relative molecular masses extremely accurately. **High resolution mass spectrometry (HRMS)** can provide particle masses to an accuracy of 1 part in 50 000. This means that masses accurate to the 4th decimal place are well within its capability.

The high resolution mass spectrometer differs from the low resolution mass spectrometer in that it incorporates an extra focussing device (see diagrams on the next page) which ensures that ions of a particular mass, entering the magnetic separator, have a very narrow spread of kinetic energies. The result of this is that the magnetic separator can perform its function much more effectively. It can separate ions of different masses more *cleanly* so providing greater resolving power. It can, for example, distinguish molecules of the gases C<sub>2</sub>H<sub>4</sub> (ethene, mass: 28.0313), CO (carbon monoxide, mass: 27.9949) and N<sub>2</sub> (nitrogen, mass: 28.0061) quite easily. Since HRMS can provide atomic and molecular masses to at least four decimal places it is possible to translate an accurate molecular mass directly into a molecular formula!



## For example,

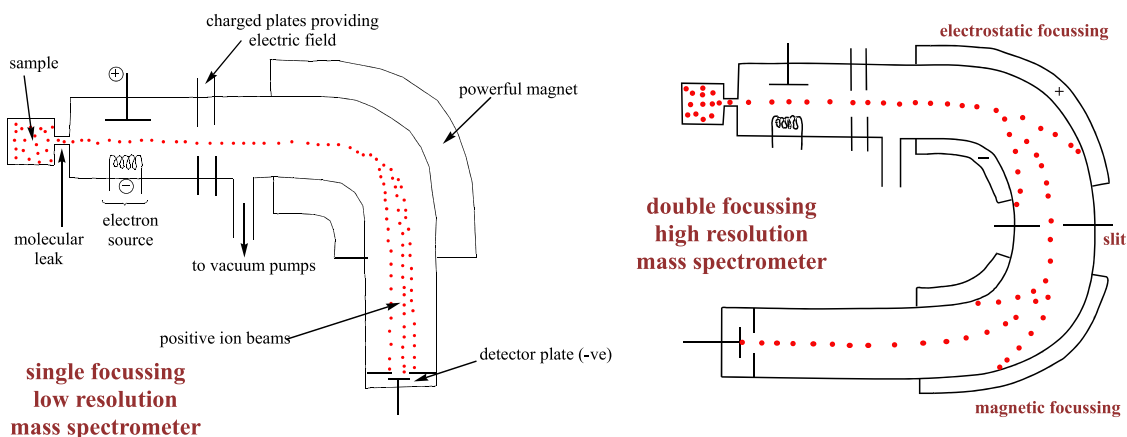
Mass spectrometry of an unknown substance gives a mass spectrum which has the following main features.



This spectrum tells us that we have an organic compound whose molecular structure contains two bromine atoms. The odd mass peak at  $m/z$  27 suggests  $C_2H_3^+$  and the triplet gives an overall molecular mass in the region of 186. This suggests a molecule with the molecular formula,  $C_2H_4Br_2$

This is confirmed by HRMS which gives molecular ion masses of 187.8679, 188.8659, & 189.8639. These masses correspond to,  $C_2H_4^{79}Br^{79}Br^+$ ,  $C_2H_4^{79}Br^{81}Br^+$ ,  $C_2H_4^{81}Br^{81}Br^+$ .

These results do not distinguish between 1,2-dibromoethane and 1,1-dibromoethane. These two molecules give very similar mass spectra differing only in the masses of the base peaks (in 1,1-dibromoethane  $m/z$  27 is usually the base peak and in 1,2-dibromoethane  $m/z$  107 is usually the base peak). However, a comparison of their infra red and nmr spectra with standard ir & nmr spectra would resolve the problem!



### (c) Visible & Ultra-violet Spectroscopy

Visible and ultra-violet light is relatively high energy electromagnetic radiation.

When absorbed by molecules or ions it causes movement of electrons between the available electronic energy levels.

The precise wavelengths of the absorbed radiation is characteristic of the molecular (or ionic) structure and bonding. By measuring these wavelengths, using a *UV/Vis spectrophotometer*, it may be possible to deduce some information about the structure of the molecule or ion.

eg,

—NO<sub>2</sub> this group absorbs strongly at 210 nm

$\diagup$  C=O  $\diagdown$  this group absorbs weakly at 195 nm

These are examples of **chromophores**,

-- that part of a molecule which absorbs vis/uv most strongly.

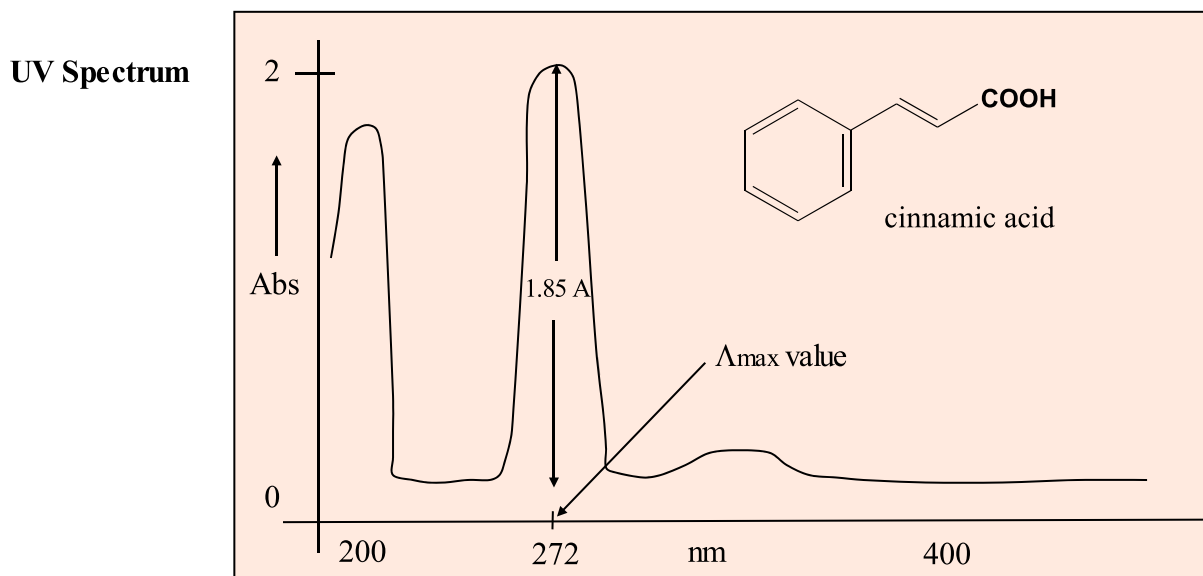
$\diagup$  C=C  $\diagdown$  C=O this group strongly at about 230 nm

Generally, the more **unsaturated** the absorbing specie the more complex and intense the absorption.

The more **conjugated** the more intense the absorption and the longer the  $\lambda_{\text{max}}$  value.

However, the spectra are usually simple containing one or two broad, intense, absorption bands.

eg,



The most important application of visible and ultra-violet spectroscopy is in **quantitative analysis**.

The absorbance is directly related to the concentration of the specie in solution.  
ie,

**Beer-Lambert Law:**

$$A = \epsilon \cdot l \cdot c$$

August Beer (1852),

Johann Heinrich Lambert (1760)

Where,  $A$  = absorbance ( $= \log(I_0/I_t)$ ) and  $\epsilon$  = molar absorptivity,  $c$  = concentration ( $\text{mol dm}^{-3}$ ),  $l$  = length of solution in the light beam (cm),  $I_0$  = intensity of the incident light,  $I_t$  = intensity of the transmitted light.

The usual procedure is to prepare a number of **standard solutions** of the substance under investigation and measure their absorbance values. Absorbances are then plotted against concentration to give a **calibration curve**.

The absorbance of the unknown solution is measured and, using the calibration curve, the corresponding concentration read off.

## (d) Nuclear Magnetic Resonance Spectroscopy (NMR).

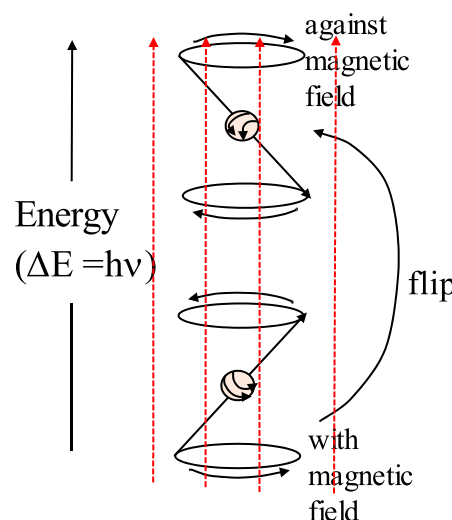
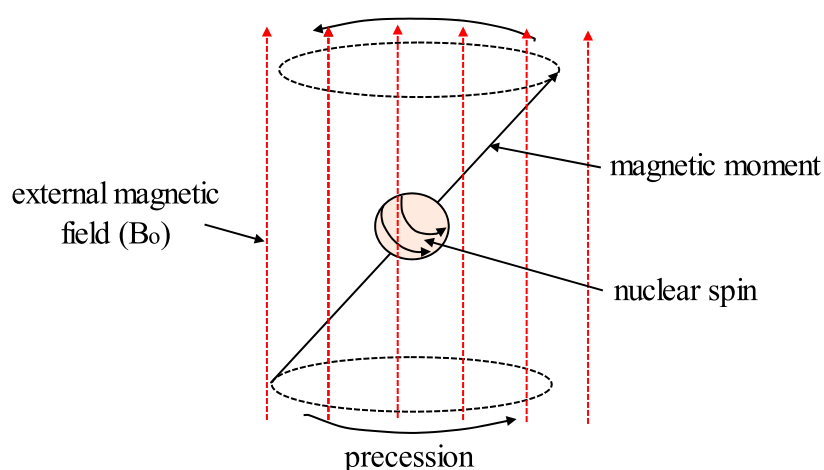
Nuclear magnetic resonance is a property of the **nucleus** of an atom.

This spectroscopic method is used to detect the atomic nuclei in molecules.

Only nuclei with odd mass and/or atomic numbers exhibit nmr.

eg,  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$

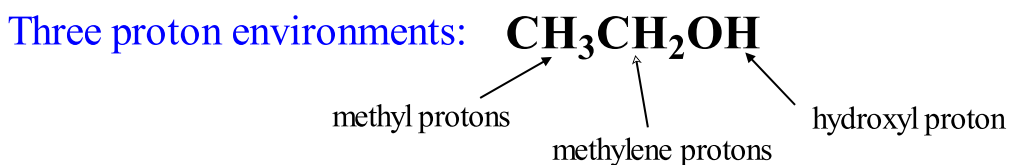
Spinning **protons**, as in organic molecules, generate a small magnetic field (like a small bar magnet). Placed in a strong, external, magnetic field they will **precess** and adopt one of two orientations - **with** or **against** the external field.



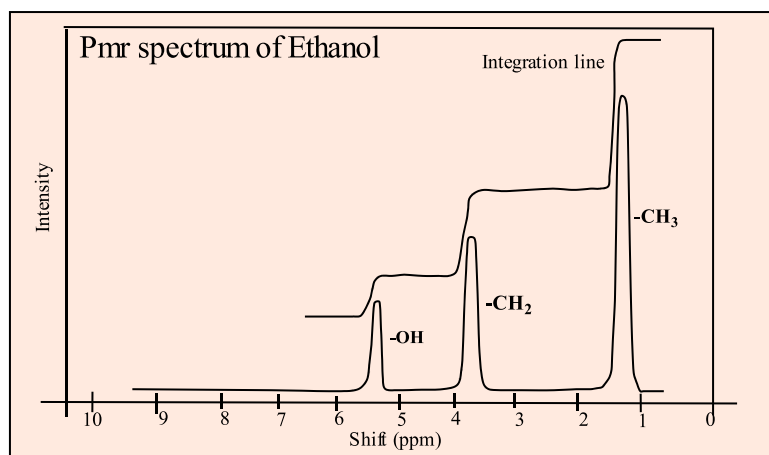
As you can imagine, the amount of energy required to flip the proton between these two orientations is very very small. Low energy electromagnetic radiation in the **radio frequency region** is sufficient to achieve this transition. A signal of about 60Mhz will cause promotion from the low energy state to the high energy state. When this occurs the protons are said to undergo **resonance**.

The precise amount of energy for resonance depends on the **type** of nucleus being examined (  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  ) and the **environment** of the nucleus.

eg, consider ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )



We expect these three sets of protons to require different amounts of energy to undergo resonance. This is indeed the case. The nmr spectrum (or in this case the **proton magnetic resonance (pmr) spectrum**) shows three distinct resonance lines (or peaks) at three different energy (or **shift**) values.



The integration line, drawn on the spectrum above the peaks, indicates the relative heights of the peaks; each step is proportional to the number of protons giving rise to the peak.

Some approximate shift values, for protons in different environments, are given in the table on the next page.

## Organic Analysis

Group	Shift (ppm)
TMS: $\text{Si}(\text{CH}_3)_4$	0.00
$\text{CH}_3\text{-C}$	1.0
$\text{CH}_3\text{-C=O}$	2.1
$\text{H}-\text{C}\equiv\text{C}-$	3.1
$\text{Ar-CH}_2\text{-}$	2.7
$\text{-O-CH}_2\text{-O-}$	3.4
$\text{C}_6\text{H}_6$	7.2
$\text{-CHO}$	9.9

Tetramethylsilane (TMS) is used as a standard.  
The shift values of the other protons are relative to  
TMS (ie, on a scale where TMS = 0.00).

### Shielded and deshielded protons:

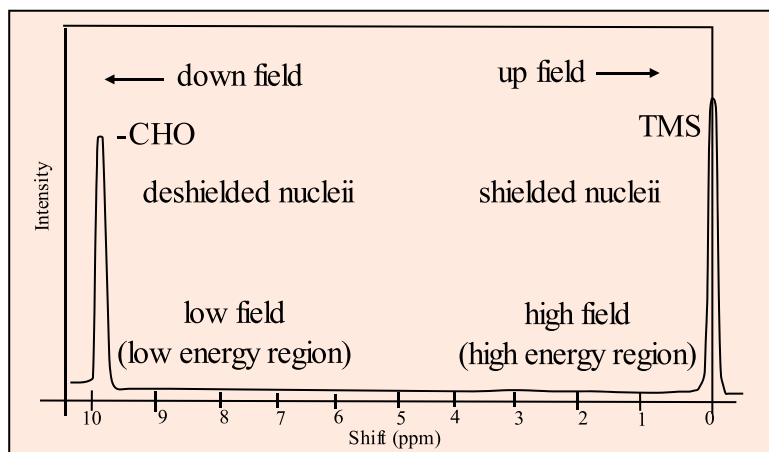
The protons in TMS are highly *shielded* due to the electron donating property of the silicon atom. On the other hand, the proton in an aldehyde group is highly *deshielded* due to the electron withdrawing property of the carbonyl group.

#### High field and low field:

The shielded protons in TMS require a large amount of energy to cause them to resonate. They produce a peak to the far right of the pmr spectrum in the *high field region*.

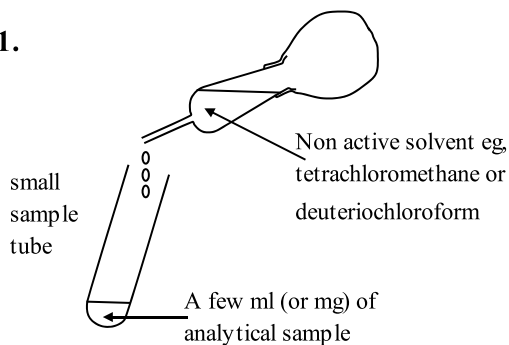
Aldehyde protons, on the other hand, are deshielded and absorb in the *low field region* to the left of the pmr spectrum.

ie,

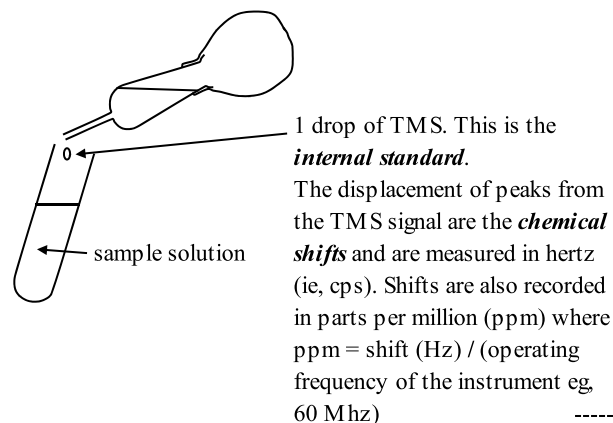


## How to obtain a PMR Spectrum

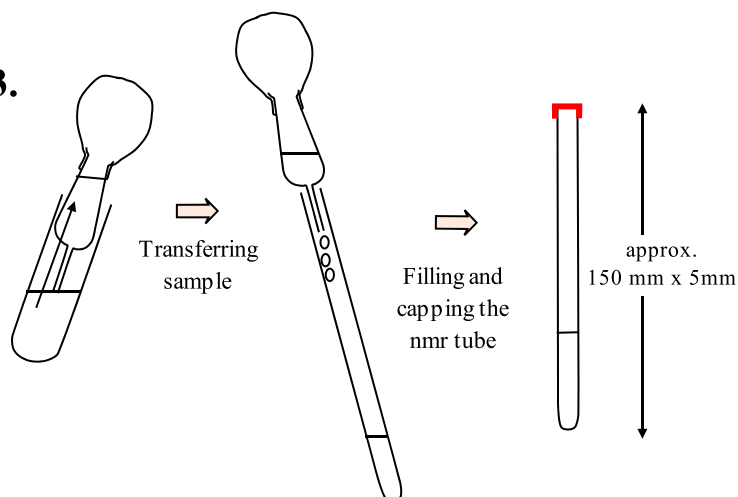
1.



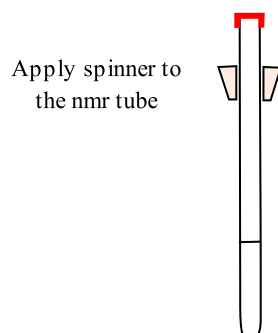
2.



3.

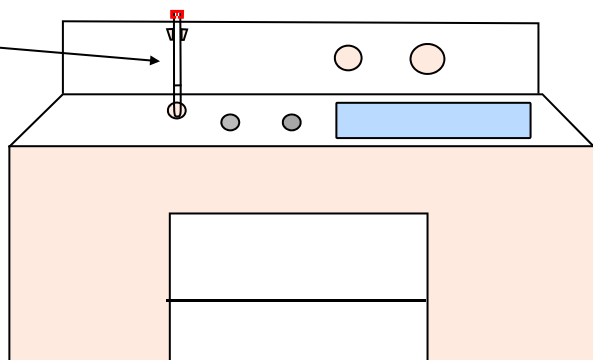


4.



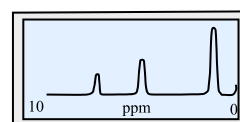
5.

Lower the nmr tube into the nmr spectrophotometer. The tube is suspended and spun between the poles of a powerful magnet (eg.  $B_0 = 1.4$  tesla)



6.

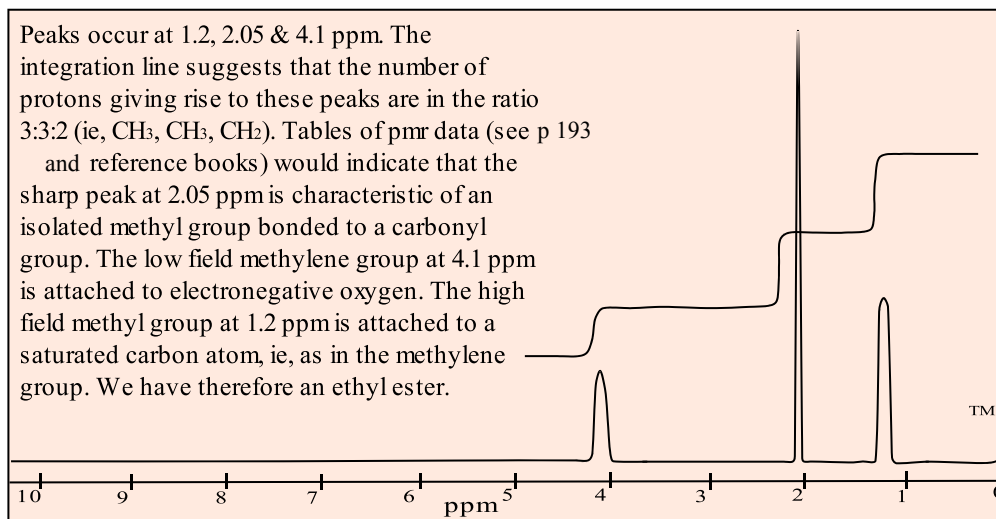
Operate instrument controls to obtain pmr spectrum of the analytical sample.



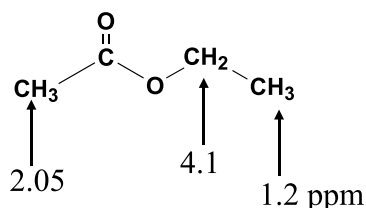
The sample tube is irradiated with 60 Mhz radiofrequency radiation and the magnetic field swept over a narrow range to cause protons in different environments to undergo resonance. As each set of protons resonate, and then return to the ground state, they emit a small radiofrequency signal which is detected and amplified and displayed on chart paper as a peak or group of peaks.

## Example 1:

The low resolution pmr spectrum of a colourless, pleasant smelling, liquid (bp 77°C, relative molecular mass = 88.1) had the following characteristics.



## Conclusion:



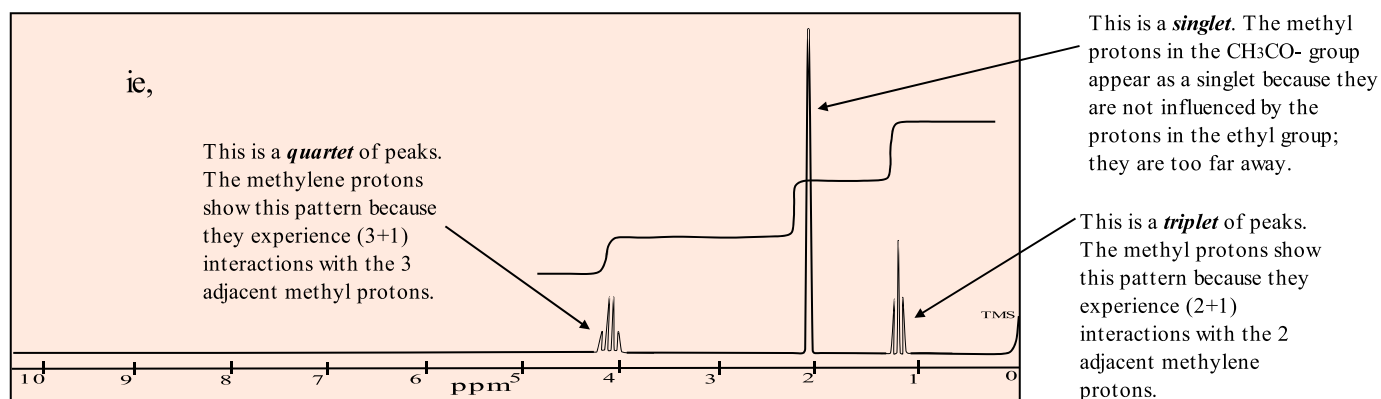
ethyl ethanoate (ethylacetate)

molecular formula = C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>  
molar mass = 88.1

## Why are some of the peaks in the low resolution pmr spectrum broad?

You may wonder why the protons in the ethyl group give rise to *broad* peaks in the above pmr spectrum? The answer is that since these protons are close together (ie, on adjacent carbon atoms) they interact magnetically and electronically and give rise to diffuse absorption peaks at *low* resolution. The ethyl protons experience what is called ***spin-spin coupling***.

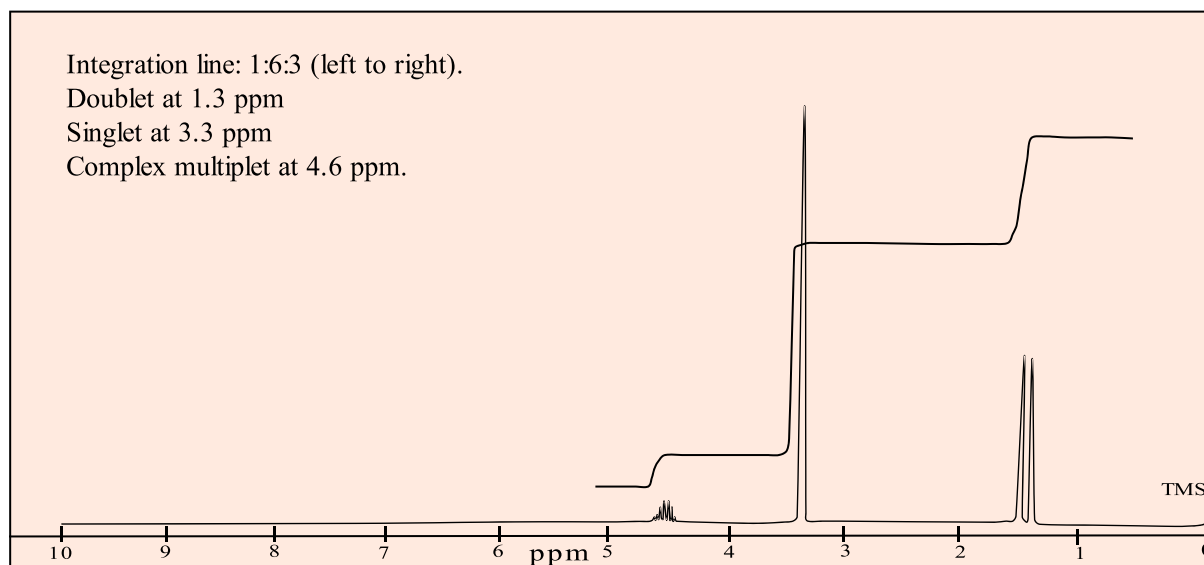
**High** resolution pmr reveals that these broad peaks are in fact closely spaced *multiplet* peaks.



These splitting or multiplet patterns are clearly very important in providing structural information about a molecule. The three-four pattern, for example, is very characteristic of an isolated ethyl group.

## Example 2.

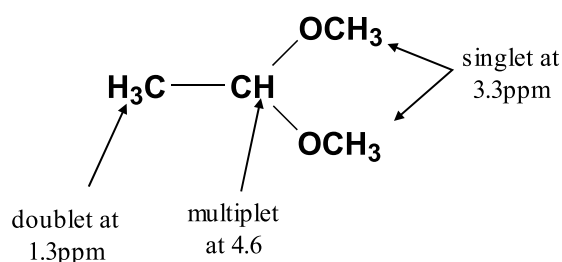
A colourless liquid compound (molar mass 90.1), bp 64°C, and slightly soluble in water gives the following pmr spectrum.



If the protons giving the peak at 1.3ppm are attached to a saturated carbon with a single proton (ie, a methine carbon), this would account for the splitting to give the doublet. It also looks as if the methine absorption is basically a quartet with some further splitting. This suggests that the protons giving the peak at 1.3ppm are in a methyl group. If this is the case the singlet at 3.3ppm is due to six equivalent protons (ie, two methyl groups in identical environments). The fairly low field shift value of 3.3ppm further suggests that the methyl groups are attached to electronegative oxygen (as in a methoxy groups  $-\text{OCH}_3$ ). The methine proton at 4.6ppm shows some additional splitting due to long range interaction with the methoxy protons.

### Conclusion:

1,1-dimethoxyethane fits the above analyses.  
 ie,



Just to summarise so far. We have methods for investigating and separating mixtures. We have chemical methods for identifying the elements in a sample of a pure substance. We have quantitative methods (chemical, mass spectrometry and uv/visible spectrophotometry for example) which enable us to deduce the % elements in a sample and the quantity of sample in a solution. Mass spectrometry can also provide the molar mass of a compound as well as additional structural information. We have nmr spectrophotometry which identifies atomic nuclei and tells us the structural environments in which these nuclei exist. This method is extremely valuable for providing information about protons and carbon-13 (& in turn, carbon-12) nuclei.

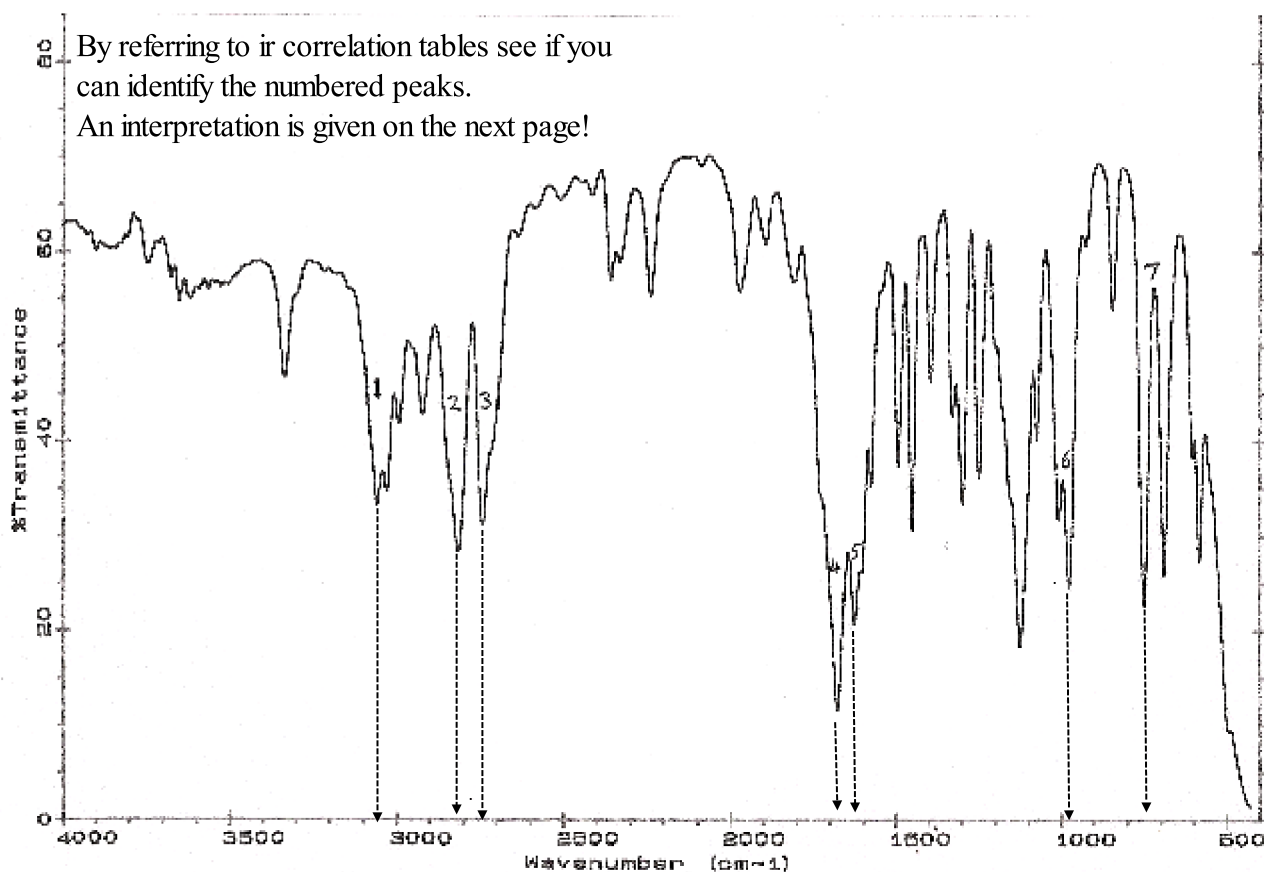


A further tool in our analytical tool kit is *infra-red spectrophotometry* (ir).

This was introduced in the Organic Chemistry II theme. However, just to remind you, it helps identify chemical bonds and functional groups. For example, the ir spectrum of an aldehyde or ketone shows very strong absorption in the region of  $1700\text{ cm}^{-1}$ . Aliphatic substances show strong absorption *just above*  $3000\text{ cm}^{-1}$  and aromatic substances show medium to strong absorption *just below*  $3000\text{ cm}^{-1}$ .

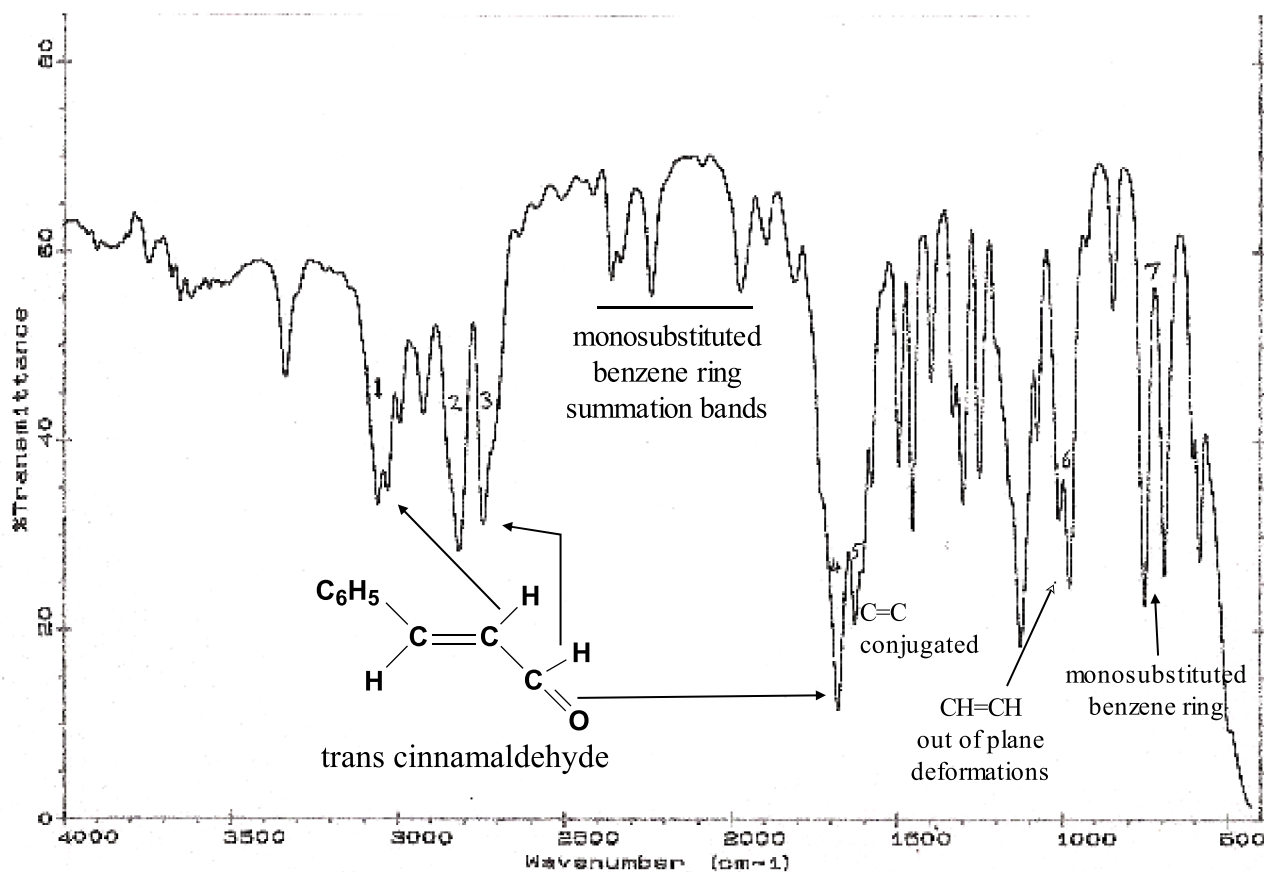
### Example:

The ir spectrum shown below is that of a simple organic compound. What can you say about its molecular structure?



### Additional analytical data:

This substance boils at  $220^{\circ}\text{C}$  with decomposition. It has the odour of cinnamon (too easy?)! Warmed with KOH solution it gives a white crystalline solid mp  $133^{\circ}\text{C}$ . Oxidised by permanganate solution it gives benzenecarbaldehyde. With semicarbazone it gives a crystalline dervative which melts at  $215^{\circ}\text{C}$ . It gives a positive result when tested with Tollen's reagent. It burns with a very smokey flame.



## Chromatography

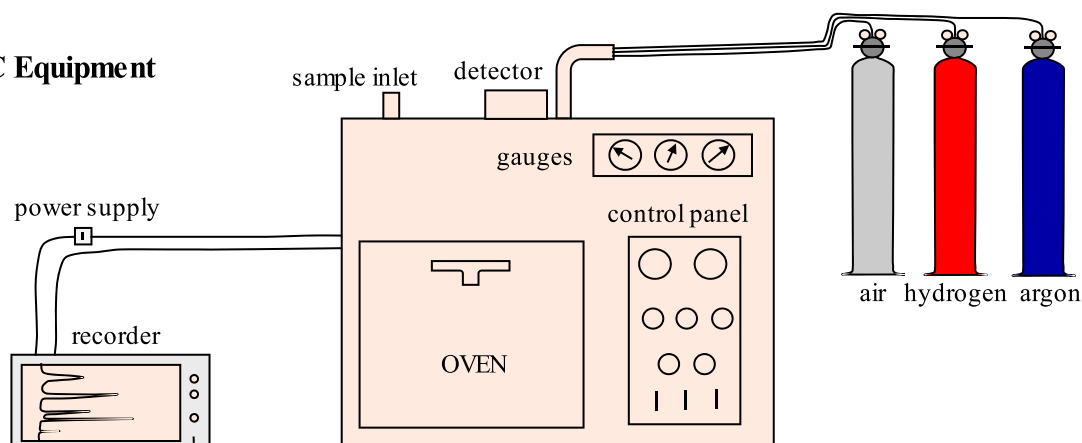
At the beginning of this section I referred to chromatography as a means of separating mixtures. Paper chromatography and simple column chromatography were illustrated.

**Gas chromatography** and **high performance liquid chromatography** are types of column chromatography linked to sophisticated instrumentation. They are powerful analytical tools.

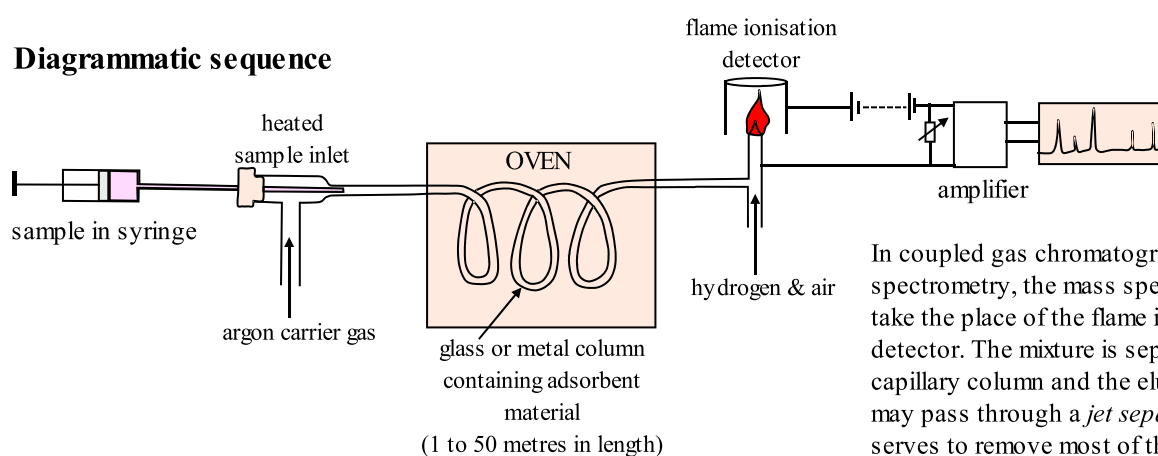
### Gas chromatography:

This technique is used to separate mixtures which can be volatilised by gentle heating. The gaseous mixture is carried through a, heated, long glass or metal column packed with a powdered material coated with inert, involatile, wax or oil known as the **stationary phase**. This stationary phase shows differing affinities for the components of the mixture with the results that the components of the mixture emerge from the chromatography column at different time intervals. The components successively pass through a detector (such as a **flame ionisation detector**) when they produce an electrical signal which is amplified and recorded as a peak on chart paper. If the separation has been successful each peak corresponds to an individual substance and the size of the peak is proportional to the amount of that substance in the original mixture. Furthermore, the time the substance takes to pass through the column (the **retention time**) is characteristic of that substance under the conditions of the chromatography. From the results of the chromatography it may be possible to give the % composition of the mixture and the identity of the components. This should certainly be possible if the gas chromatograph is linked to a mass spectrometer (ie, as in gc-ms).

## GLC Equipment



## Diagrammatic sequence



In coupled gas chromatography/mass spectrometry, the mass spectrometer can take the place of the flame ionisation detector. The mixture is separated on a capillary column and the eluant from this may pass through a *jet separator*, which serves to remove most of the carrier gas, and then into the mass spectrometer. The mass spectrometer can respond very quickly and provide mass spectra of the separated components. The whole process is computer controlled.

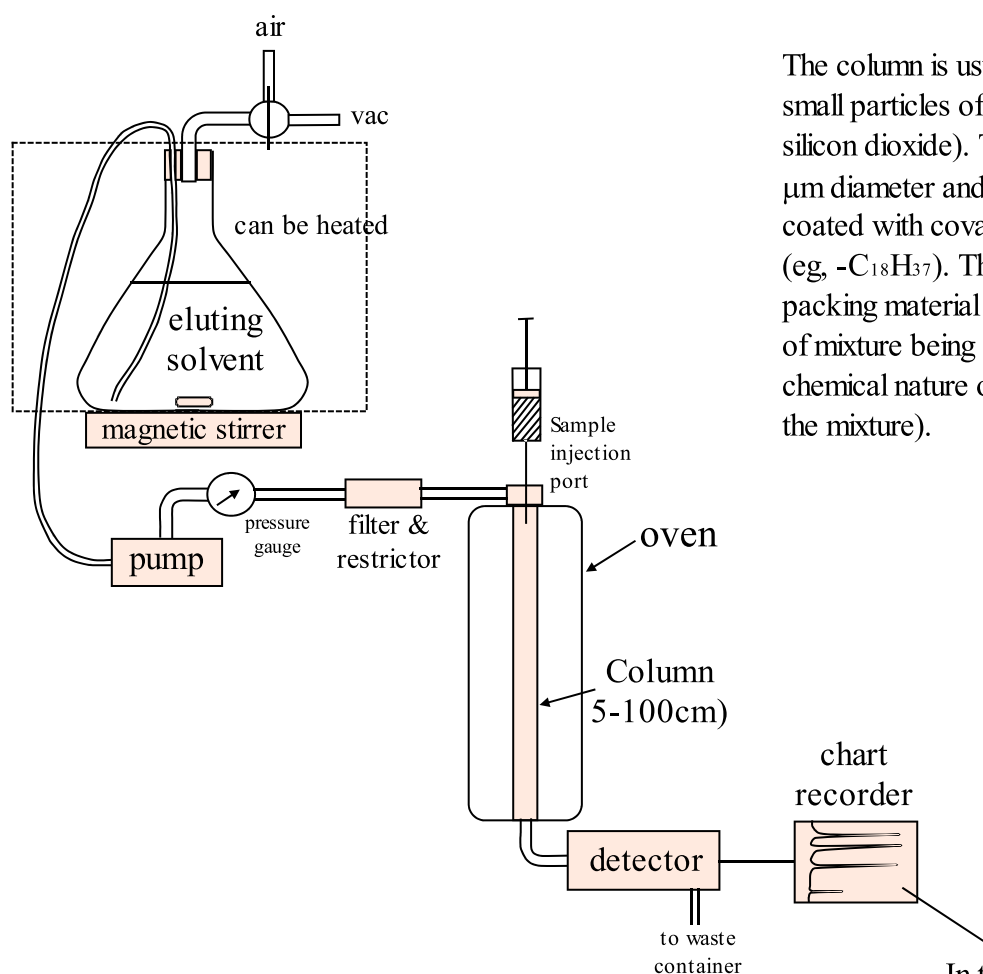
## High Performance Liquid Chromatography

The difference between ordinary liquid column chromatography, illustrated earlier, and high performance liquid chromatography (HPLC) is that the latter is operated at pressure well above atmospheric. The eluant (the eluting solvent), instead of being allowed to flow slowly through the column under the influence of gravity, is forced through by means of a pump. Pressures in excess of 4000 psi (285 atm) are often used. To withstand these pressures the chromatography columns are usually made of steel.

As the separated components come off the column they enter the detector. A variety of detectors are available depending on the type of sample being analysed. The most popular are the UV detector and the general purpose refractive index detector.

As with gas liquid chromatography, HPLC can be linked to a mass spectrometer (LC/MS).

## Diagrammatic representation of an HPLC set-up:



The column is usually packed with very small particles of silica gel (hydrated silicon dioxide). The particles are 5-10  $\mu\text{m}$  diameter and may or may not be coated with covalently bonded groups (eg,  $-\text{C}_{18}\text{H}_{37}$ ). The nature of the packing material depends on the type of mixture being separated (ie, the chemical nature of the constituents of the mixture).

In the ideal situation, each peak corresponds to a single substance. The retention time is characteristic of the substance and the area under the peak is proportional to the % of that substance in the original mixture.